Manahan, Stanley E. "Frontmatter"
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PREFACE TO THE SECOND EDITION

Fundamentals of Environmental Chemistry, 2nd edition, is written with two major objectives in mind. The first of these is to provide a reader having little or no background in chemistry with the fundamentals of chemistry needed for a trade, profession, or curriculum of study that requires a basic knowledge of these topics. The second objective of the book is to provide a basic coverage of modern environmental chemistry. This is done within a framework of industrial ecology and an emerging approach to chemistry that has come to be known as "green chemistry."

Virtually everyone needs some knowledge of chemistry. Unfortunately, this vital, interesting discipline "turns off" many of the very people who need a rudimentary knowledge of it. There are many reasons that this is so. For example, "chemophobia," an unreasoned fear of insidious contamination of food, water, and air with chemicals at undetectable levels that may cause cancer and other maladies is widespread among the general population. The language of chemistry is often made too complex so that those who try to learn it retreat from concepts such as moles, orbitals, electronic configurations, chemical bonds, and molecular structure before coming to realize that these ideas are comprehensible and even interesting and useful.

Fundamentals of Environmental Chemistry is designed to be simple and understandable, and it is the author's hope that readers will find it interesting and applicable to their own lives. Without being overly simplistic or misleading, it seeks to present chemical principles in ways that even a reader with a minimal background in, or no particular aptitude for, science and mathematics can master the material in it and apply it to a trade, profession, or course of study.

One of the ways in which *Environmental Chemistry Fundamentals* presents chemistry in a "reader-friendly" manner is through a somewhat unique organizational structure. In the first few pages of Chapter 1, the reader is presented with a "mini-course" in chemistry that consists of the most basic concepts and terms needed to really begin to understand chemistry. To study chemistry, it is necessary to know a few essential things—what an atom is, what is meant by elements, chemical formulas, chemical bonds, molecular mass. With these terms defined in very basic

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ways it is possible to go into more detail on chemical concepts without having to assume—as many introductory chemistry books do somewhat awkwardly—that the reader knows nothing of the meaning of these terms.

Chapter 2 discusses matter largely on the basis of its physical nature and behavior, introducing physical and chemical properties, states of matter, the mole as a quantity of matter, and other ideas required to visualize chemical substances as physical entities. Chapters 3–5 cover the core of chemical knowledge constructed as a language in which elements and the atoms of which they are composed (Chapter 3) are presented as letters of an alphabet, the compounds made up of elements (Chapter 4) are analogous to words, the reactions by which compounds are synthesized and changed (Chapter 5) are like sentences in the chemical language, and the mathematical aspects hold it all together quantitatively. Chapters 6–8 constitute the remainder of material that is usually regarded as essential material in general chemistry. Chapter 9 presents a basic coverage of organic chemistry. Although this topic is often ignored at the beginning chemistry level, those who deal with the real world of environmental pollution, hazardous wastes, agricultural science, and other applied areas quickly realize that a rudimentary understanding of organic chemistry is essential. Chapter 10 covers biological chemistry, an area essential to understanding later material dealing with environmental and toxicological chemistry.

Beyond Chapter 10, the book concentrates on environmental chemistry. Traditionally, discussion of environmental science has been devoted to the four traditional spheres—the hydrosphere, atmosphere, geosphere, and biosphere—that is, water, air, land, and life. It has usually been the case that, when mentioned at all in environmental science courses, human and industrial activities have been presented in terms of pollution and detrimental effects on the environment. *Fundamentals of Environmental Chemistry* goes beyond this narrow focus and addresses a fifth sphere of the environment, the anthrosphere, consisting of the things that humans make, use, and do. In taking this approach, it is recognized that humans have vast effects upon the environment and that they will use the other environmental spheres and the materials, energy, and life forms in them for perceived human needs. The challenge before humankind is to integrate the anthrosphere into the total environment and to direct human efforts toward the preservation and enhancement of the environment, rather than simply its exploitation. Environmental chemistry has a fundamental role in this endeavor, and this book is designed to assist the reader with the basic tools required to use environmental chemistry to enhance the environment upon which we all ultimately depend for our existence and well-being.

Chapters 11–13 address the environmental chemistry of the hydrosphere. Chapter 11 discusses the fundamental properties of water, water supply and distribution, properties of bodies of water, and basic aquatic chemistry, including acid-base behavior, phase interactions, oxidation-reduction, chelation, and the important influences of bacteria, algae, and other life forms on aquatic chemistry. Chapter 12 deals specifically with water pollution and Chapter 13 with water treatment.

Chapter 14 introduces the atmosphere and atmospheric chemistry, including the key concept of photochemistry. It discusses stratification of the atmosphere, Earth's crucial energy balance between incoming solar energy and outgoing infrared energy, and weather and climate as they are driven by redistribution of energy and water in

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the atmosphere. Inorganic air pollutants, including nitrogen and sulfur oxides, carbon monoxide, and carbon dioxide (potentially a "pollutant" if excessive levels lead to detrimental greenhouse warming) are discussed in Chapter 14. Organic air pollutants and photochemical smog are the topics of Chapter 15.

The geosphere is addressed in Chapters 17 and 18. Chapter 17 is a discussion of the composition and characteristics of the geosphere. Chapter 18 deals with soil and agriculture and addresses topics such as conservation tillage and the promise and potential pitfalls of genetically modified crops and food.

Chapters 19–22 discuss anthrospheric aspects of environmental chemistry. Chapter 19 outlines industrial ecology as it relates to environmental chemistry. Chapter 20 covers the emerging area of "green chemistry," defined as the sustainable exercise of chemical science and technology within the framework of good practice of industrial ecology so that the use and handling of hazardous substances are minimized and such substances are never released to the environment. Chapter 21 covers the nature, sources, and chemistry of hazardous substances. Chapter 22 addresses the reduction, treatment, and disposal of hazardous wastes within a framework of the practice of industrial ecology.

Aspects of the biosphere are covered in several parts of the book. Chapter 10 provides a basic understanding of biochemistry as it relates to environmental chemistry. The influence of organisms on the hydrosphere is discussed in Chapters 11–13. Chapter 23 deals specifically with toxicological chemistry.

Chapter 24 covers resources, both renewable and nonrenewable, as well as energy from fossil and renewable sources. The last two chapters outline analytical chemistry. Chapter 25 presents the major concepts and techniques of analytical chemistry. Chapter 26 discusses specific aspects of environmental chemical analysis, including water, air, and solid-waste analysis, as well as the analysis of xenobiotic species in biological systems.

The author welcomes comments and questions from readers. He can be reached by e-mail at manahans@missouri.edu.

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Professor Manahan is the author or coauthor of approximately 100 journal articles in environmental chemistry and related areas. In addition to *Fundamentals of Environmental Chemistry*, 2nd ed., he is the author of *Environmental Chemistry*, 7th ed. (2000, Lewis Publishers), which has been published continuously in various editions since, 1972. Other books that he has written are *Industrial Ecology: Environmental Chemistry and Hazardous Waste* (Lewis Publishers, 1999), *Environmental Science and Technology*(Lewis Publishers, 1997), *Toxicological Chemistry*, 2nd ed. (Lewis Publishers, 1992), *Hazardous Waste Chemistry, Toxicology and Treatment* (Lewis Publishers, 1992), *Quantitative Chemical Analysis*, Brooks/Cole, 1986), and *General Applied Chemistry*, 2nd ed. (Willard Grant Press, 1982).

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1 INTRODUCTION TO CHEMISTRY

1.1 CHEMISTRY AND ENVIRONMENTAL CHEMISTRY

Chemistry is defined as the science of matter. Therefore, it deals with the air we breathe, the water we drink, the soil that grows our food, and vital life substances and processes. Our own bodies contain a vast variety of chemical substances and are tremendously sophisticated chemical factories that carry out an incredible number of complex chemical processes.

There is a tremendous concern today about the uses—and particularly the misuses—of chemistry as it relates to the environment. Ongoing events serve as constant reminders of threats to the environment ranging from individual exposures to toxicants to phenomena on a global scale that may cause massive, perhaps catastrophic, alterations in climate. These include, as examples, evidence of a perceptible warming of climate; record weather events—particularly floods—in the United States in the 1990s; and air quality in Mexico City so bad that it threatens human health. Furthermore, large numbers of employees must deal with hazardous substances and wastes in laboratories and the workplace. All such matters involve environmental chemistry for understanding of the problems and for arriving at solutions to them.

Environmental chemistry is that branch of chemistry that deals with the origins, transport, reactions, effects, and fates of chemical species in the water, air, earth, and living environments and the influence of human activities thereon.[1] A related discipline, **toxicological chemistry**, is the chemistry of toxic substances with emphasis upon their interaction with biologic tissue and living systems.[2] Besides its being an essential, vital discipline in its own right, environmental chemistry provides an excellent framework for the study of chemistry, dealing with "general chemistry," organic chemistry, chemical analysis, physical chemistry, photochemistry, geochemistry, and biological chemistry. By necessity it breaks down the barriers that tend to compartmentalize chemistry as it is conventionally addressed. Therefore, this book is written with two major goals—to provide an overview of chemical science within an environmental chemistry framework and to provide the basics of environmental

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chemistry for those who need to know about this essential topic for their professions or for their overall education.

1.2 A MINI-COURSE IN CHEMISTRY

It is much easier to learn chemistry if one already knows some chemistry! That is, in order to go into any detail on any chemical topic, it is extremely helpful to have some very rudimentary knowledge of chemistry as a whole. For example, a crucial part of chemistry is an understanding of the nature of chemical compounds, the chemical formulas used to describe them, and the chemical bonds that hold them together; these are topics addressed in Chapter 3 of this book. However, to understand these concepts, it is very helpful to know some things about the chemical reactions by which chemical compounds are formed, as addressed in Chapter 4. To work around this problem, Chapter 1 provides a highly condensed, simplified, but meaningful overview of chemistry to give the reader the essential concepts and terms required to understand more-advanced chemical material.

1.3 THE BUILDING BLOCKS OF MATTER

All matter is composed of only about a hundred fundamental kinds of matter called **elements**. Each element is made up of very small entities called **atoms**; all atoms of the same element behave identically chemically. The study of chemistry, therefore, can logically begin with elements and the atoms of which they are composed.

Subatomic Particles and Atoms

Figure 1.1 represents an atom of deuterium, a form of the element hydrogen. It is seen that such an atom is made up of even smaller **subatomic particles**—positively charged **protons**, negatively charged **electrons**, and uncharged (neutral) **neutrons.** Protons and neutrons have relatively high masses compared with electrons and are contained in the positively charged **nucleus** of the atom. The nucleus has essentially all the mass, but occupies virtually none of the volume, of

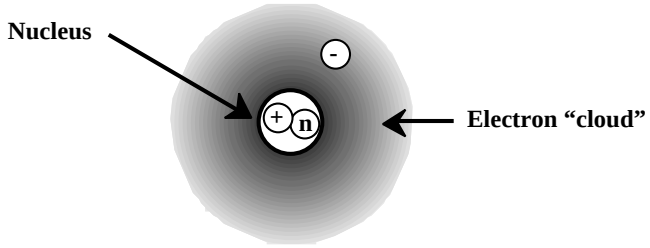


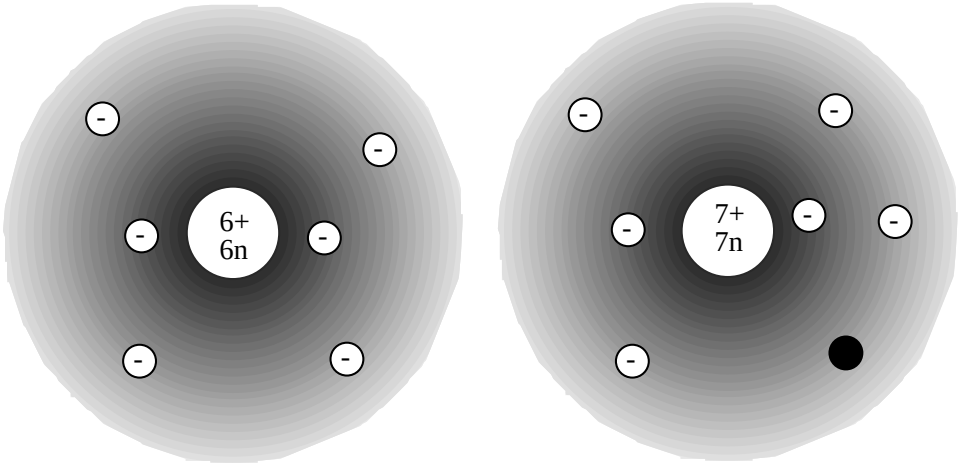
Figure 1.1 Representation of a deuterium atom. The nucleus contains one proton (+) and one neutron (n). The electron (-) is in constant, rapid motion around the nucleus, forming a cloud of negative electrical charge, the density of which drops off with increasing distance from the nucleus.

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the atom. An uncharged atom has the same number of electrons as protons. The electrons in an atom are contained in a cloud of negative charge around the nucleus that occupies most of the volume of the atom.

Atoms and Elements

All of the literally millions of different substances are composed of only around 100 elements. Each atom of a particular element is chemically identical to every other atom and contains the same number of protons in its nucleus. This number of protons in the nucleus of each atom of an element is the **atomic number** of the element. Atomic numbers are integers ranging from 1 to more than 100, each of which denotes a particular element. In addition to atomic numbers, each element has a name and a **chemical symbol**, such as carbon, C; potassium, K (for its Latin name kalium); or cadmium, Cd. In addition to atomic number, name, and chemical symbol, each element has an **atomic mass** (atomic weight). The atomic mass of each element is the average mass of all atoms of the element, including the various isotopes of which it consists. The **atomic mass unit**, **u** (also called the **dalton**), is used to express masses of individual atoms and molecules (aggregates of atoms). These terms are summarized in Figure 1.2.



An atom of carbon, symbol C. Each C atom has 6 protons (+) in its nucleus, so the atomic number of C is 6. The atomic mass of C is 12.

An atom of nitrogen, symbol N. Each N atom has 7 protons (+) in its nucleus, so the atomic number of N is 7. The atomic mass of N is 14.

Figure 1.2 Atoms of carbon and nitrogen

Although atoms of the same element are *chemically* identical, atoms of most elements consist of two or more **isotopes** that have different numbers of neutrons in their nuclei. Some isotopes are **radioactive isotopes** or **radionuclides**, which have unstable nuclei that give off charged particles and gamma rays in the form of **radioactivity**. This process of **radioactive decay** changes atoms of a particular element to atoms of another element.

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Throughout this book reference is made to various elements. A list of the known elements is given on page 120 at the end of Chapter 3. Fortunately, most of the chemistry covered in this book requires familiarity with only about 25 or 30 elements. An abbreviated list of a few of the most important elements that the reader should learn at this point is given in Table 1.1.

Table 1.1 List of Some of the More Important Common Elements

Element	Symbol	Atomic Number	Atomic Mass (relative to carbon-12)
Argon	Ar	18	39.948
Bromine	Br	35	79.904
Calcium	Ca	20	40.08
Carbon	C	6	12.01115
Chlorine	Cl	17	35.453
Copper	Cu	29	63.546
Fluorine	F	9	18.998403
Helium	He	2	4.00260
Hydrogen	H	1	1.0080
Iron	Fe	26	55.847
Magnesium	Mg	12	24.305
Mercury	Hg	80	200.59
Neon	Ne	10	20.179
Nitrogen	N	7	14.0067
Oxygen	O	8	15.9994
Potassium	K	19	39.0983
Silicon	Si	14	28.0855
Sodium	Na	11	22.9898
Sulfur	S	16	32.06

The Periodic Table

When elements are considered in order of increasing atomic number, it is observed that their properties are repeated in a periodic manner. For example, elements with atomic numbers 2, 10, and 18 are gases that do not undergo chemical reactions and consist of individual molecules, whereas those with atomic numbers larger by one—3, 11, and 19—are unstable, highly reactive metals. An arrangement of the elements in a manner that reflects this recurring behavior is known as the **periodic table** (Figure 1.3). The periodic table is extremely useful in understanding chemistry and predicting chemical behavior. The entry for each element in the periodic table gives the element's atomic number, name, symbol, and atomic mass. More-detailed versions of the table include other information as well.

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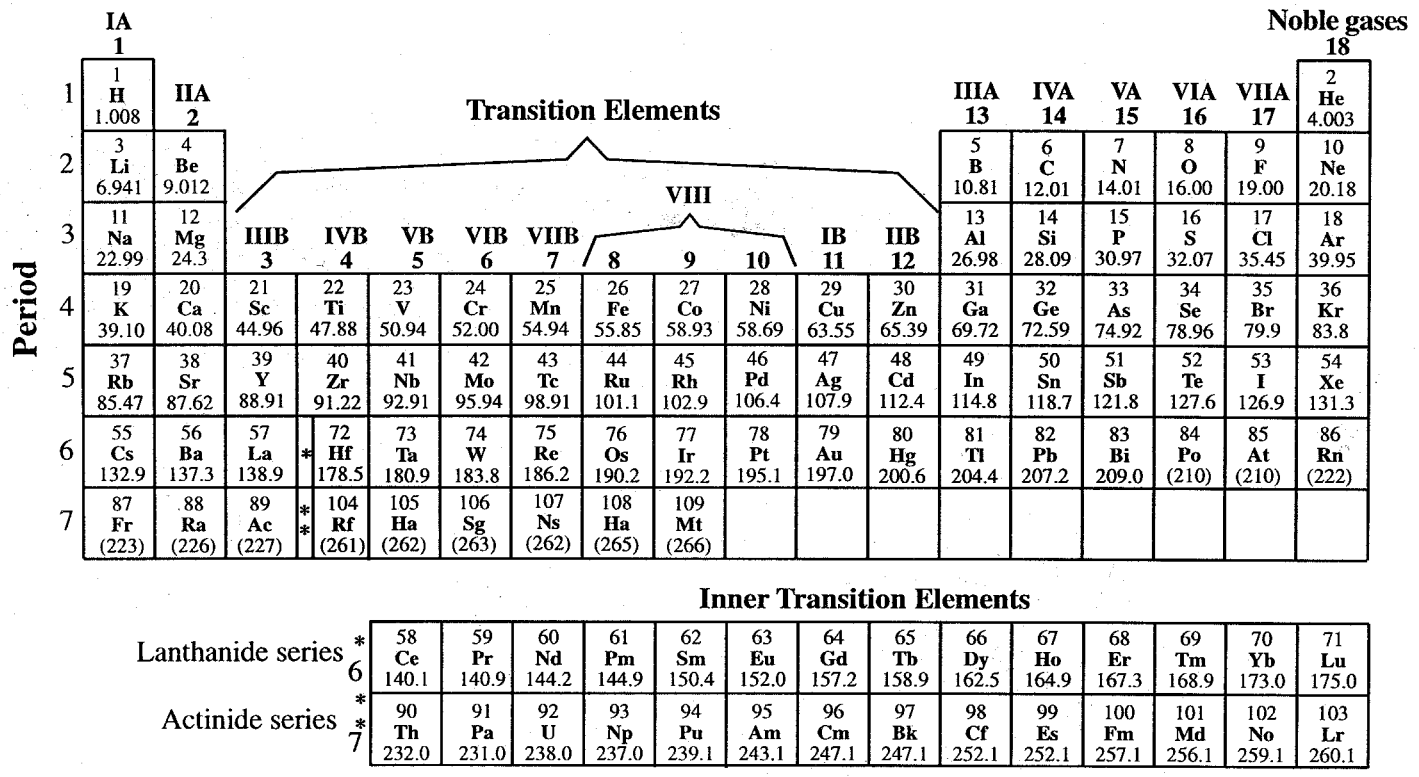


Figure 1.3 The periodic table of the elements.

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The periodic table gets its name from the fact that the properties of elements are repeated periodically in going from left to right across a horizontal row of elements. The table is arranged such that an element has properties similar to those of other elements above or below it in the table. Elements with similar chemical properties are called **groups** of elements and are contained in vertical columns in the periodic table.

1.4. CHEMICAL BONDS AND COMPOUNDS

Only a few elements, particularly the noble gases, exist as individual atoms; most atoms are joined by chemical bonds to other atoms. This can be illustrated very simply by elemental hydrogen, which exists as **molecules**, each consisting of 2 H atoms linked by a **chemical bond** as shown in Figure 1.4. Because hydrogen molecules contain 2 H atoms, they are said to be diatomic and are denoted by the **chemical formula** H_2. The H atoms in the H_2 molecule are held together by a **covalent bond** made up of 2 electrons, each contributed by one of the H atoms, and shared between the atoms.

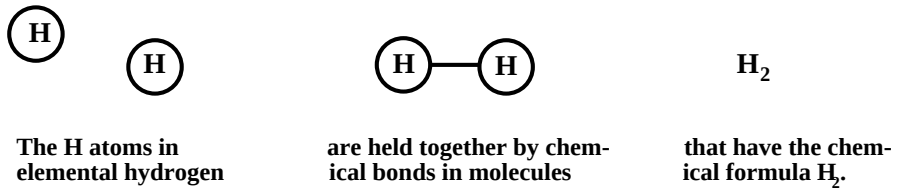


Figure 1.4 Molecule of H_2.

Chemical Compounds

Most substances consist of two or more elements joined by chemical bonds. As an example, consider the chemical combination of the elements hydrogen and oxygen shown in Figure 1.5. Oxygen, chemical symbol O, has an atomic number of 8 and an atomic mass of 16.00 and exists in the elemental form as diatomic molecules of O_2. Hydrogen atoms combine with oxygen atoms to form molecules in which 2 H atoms are bonded to 1 O atom in a substance with a chemical formula of H_2O (water). A substance such as H_2O that consists of a chemically bonded com-

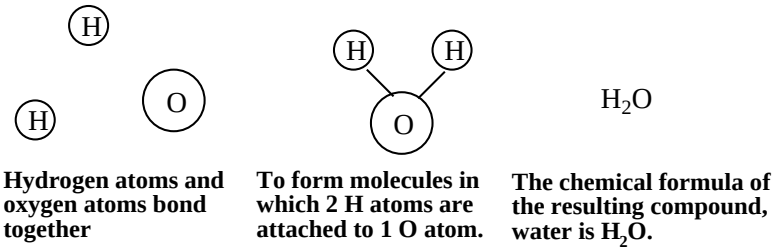


Figure 1.5 A molecule of water, H_2O, formed from 2 H atoms and 1 O atom held together by chemical bonds.

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bination of two or more elements is called a **chemical compound**. (A chemical compound is a substance that consists of atoms of two or more different elements bonded together.) In the chemical formula for water the letters H and O are the chemical symbols of the two elements in the compound and the subscript 2 indicates that there are 2 H atoms per O atom. (The absence of a subscript after the O denotes the presence of just 1 O atom in the molecule.) Each of the chemical bonds holding a hydrogen atom to the oxygen atom in the water molecule is composed of two electrons shared between the hydrogen and oxygen atoms.

Ionic Bonds

As shown in Figure 1.6, the transfer of electrons from one atom to another produces charged species called **ions**. Positively charged ions are called **cations** and negatively charged ions are called **anions**. Ions that make up a solid compound are held together by **ionic bonds** in a **crystalline lattice** consisting of an ordered arrangement of the ions in which each cation is largely surrounded by anions and each anion by cations. The attracting forces of the oppositely charged ions in the crystalline lattice constitute the ionic bonds in the compound.

The formation of the ionic compound magnesium oxide is shown in Figure 1.6. In naming this compound, the cation is simply given the name of the element from which it was formed, magnesium. However, the ending of the name of the anion, ox*ide*, is different from that of the element from which it was formed, ox*ygen.*

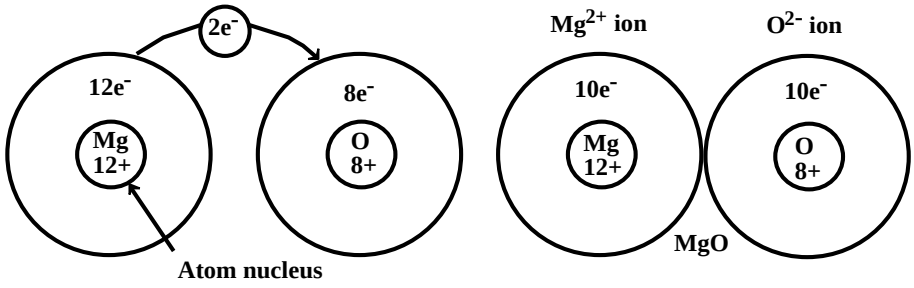
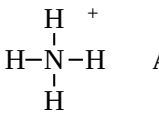


Figure 1.6 Ionic bonds are formed by the transfer of electrons and the mutual attraction of oppositely charged ions in a crystalline lattice.

Rather than individual atoms that have lost or gained electrons, many ions are groups of atoms bonded together covalently and having a net charge. A common example of such an ion is the ammonium ion, NH_4^+,



Ammonium ion, NH_4^+

consisting of 4 hydrogen atoms covalently bonded to a single nitrogen (N) atom and having a net electrical charge of +1 for the whole cation.

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Summary of Chemical Compounds and the Ionic Bond

The preceding several pages have just covered some material on chemical compounds and bonds that are essential to understand chemistry. To summarize, these are the following:

- Atoms of two or more different elements can form *chemical bonds* with each other to yield a product that is entirely different from the elements.
- Such a substance is called a *chemical compound.*
- The *formula* of a chemical compound gives the symbols of the elements and uses subscripts to show the relative numbers of atoms of each element in the compound.
- *Molecules* of some compounds are held together by *covalent bonds* consisting of shared electrons.
- Another kind of compound consists of *ions* composed of electrically charged atoms or groups of atoms held together by *ionic bonds* that exist because of the mutual attraction of oppositely charged ions.

Molecular Mass

The average mass of all molecules of a compound is its **molecular mass** (formerly called molecular weight). The molecular mass of a compound is calculated by multiplying the atomic mass of each element by the relative number of atoms of the element, then adding all the values obtained for each element in the compound. For example, the molecular mass of NH_3 is 14.0 + 3 x 1.0 = 17.0. As another example consider the following calculation of the molecular mass of ethylene, C_2H_4.

1. The chemical formula of the compound is C_2H_4.
2. Each molecule of C_2H_4 consists of 2 C atoms and 4 H atoms.
3. From the periodic table or Table 1.1, the atomic mass of C is 12.0 and that of H is 1.0.
4. Therefore, the molecular mass of C_2H_4 is

$$\underbrace{12.0 + 12.0}_{\text{From 2 C atoms}} + \underbrace{1.0 + 1.0 + 1.0 + 1.0}_{\text{From 4 H atoms}} = 28.0$$

1.5. CHEMICAL REACTIONS AND EQUATIONS

Chemical reactions occur when substances are changed to other substances through the breaking and formation of chemical bonds. For example, water is produced by the chemical reaction of hydrogen and oxygen:

Hydrogen plus oxygen yields water

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Chemical reactions are written as **chemical equations**. The chemical reaction between hydrogen and water is written as the **balanced chemical equation**

$$2H_2 + O_2 \rightarrow 2H_2O \quad (1.5.1)$$

in which the arrow is read as "yields" and separates the hydrogen and oxygen **reactants** from the water **product**. Note that because elemental hydrogen and elemental oxygen occur as *diatomic molecules* of H_2 and O_2, respectively, it is necessary to write the equation in a way that reflects these correct chemical formulas of the elemental form. All correctly written chemical equations are **balanced**, in that *they must show the same number of each kind of atom on both sides of the equation*. The equation above is balanced because of the following:

On the left

- There are 2 H_2 *molecules*, each containing 2 H *atoms* for a total of 4 H atoms on the left.
- There is 1 O_2 *molecule*, containing 2 O *atoms* for a total of 2 O atoms on the left.

On the right

- There are 2 H_2O *molecules* each containing 2 H *atoms* and 1 O atom for a total of 4 H atoms and 2 O atoms on the right.

The process of balancing chemical equations is relatively straightforward for simple equations. It is discussed in Chapter 4.

1.6. NUMBERS IN CHEMISTRY: EXPONENTIAL NOTATION

An essential skill in chemistry is the ability to handle numbers, including very large and very small numbers. An example of the former is Avogadro's number, which is discussed in detail in Chapters 2 and 3. Avogadro's number is a way of expressing quantities of entities such as atoms or molecules and is equal to 602,000,000,000,000,000,000,000. A number so large written in this decimal form is very cumbersome to express and very difficult to handle in calculations. It can be expressed much more conveniently in exponential notation. Avogadro's number in exponential notation is 6.02×10^{23}. It is put into decimal form by moving the decimal in 6.02 to the right by 23 places. Exponential notation works equally well to express very small numbers, such as 0.000,000,000,000,000,087. In exponential notation this number is 8.7×10^{-17}. To convert this number back to decimal form, the decimal point in 8.7 is simply moved 17 places to the left.

A number in exponential notation consists of a *digital number* equal to or greater than exactly 1 and less than exactly 10 (examples are 1.00000, 4.3, 6.913, 8.005, 9.99999) multiplied by a *power of 10* (10^{-17}, 10^{13}, 10^{-5}, 10^{3}, 10^{23}). Some examples of numbers expressed in exponential notation are given in Table 1.2. As seen in the second column of the table, a positive power of 10 shows the number of times that the digital number is multiplied by 10 and a negative power of 10 shows

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the number of times that the digital number is divided by 10.

Table 1.2 Numbers in Exponential and Decimal Form

Exponential form of number		Places decimal moved for decimal form	Decimal form
$1.37 \times 10^5 =$	$1.37 \times 10 \times 10 \times 10 \times 10 \times 10$	→ 5 places	137,000
$7.19 \times 10^7 =$	$7.19 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10 \times 10$	→ 7 places	71,900,000
$3.25 \times 10^{-2} =$	$3.25/(10 \times 10)$	← 2 places	0.0325
$2.6 \times 10^{-6} =$	$2.6/(10 \times 10 \times 10 \times 10 \times 10 \times 10)$	← 6 places	0.000 0026
$5.39 \times 10^{-5} =$	$5.39/(10 \times 10 \times 10 \times 10 \times 10)$	← 5 places	0.000 0539

Addition and Subtraction of Exponential Numbers

An electronic calculator keeps track of exponents automatically and with total accuracy. For example, getting the sum $7.13 \times 10^3 + 3.26 \times 10^4$ on a calculator simply involves the following sequence:

[7.13 EE3] [+] [3.26 EE4] [=] [3.97 EE4]

where 3.97 EE4 stands for 3.97×10^4. To do such a sum manually, the largest number in the sum should be set up in the standard exponential notation form and each of the other numbers should be taken to the same power of 10 as that of the largest number as shown, below for the calculation of $3.07 \times 10^{-2} - 6.22 \times 10^{-3} + 4.14 \times 10^{-4}$:

3.07×10^{-2} (largest number, digital portion between 1 and 10)
$- 0.622 \times 10^{-2}$ (same as 6.22×10^{-3})
$+ 0.041 \times 10^{-2}$ (same as 4.1×10^{-4})

Answer: 2.49×10^{-2}

Multiplication and Division of Exponential Numbers

As with addition and subtraction, multiplication and division of exponential numbers on a calculator or computer is simply a matter of (correctly) pushing buttons. For example, to solve

$$\frac{1.39 \times 10^{-2} \times 9.05 \times 10^8}{3.11 \times 10^4}$$

on a calculator, the sequence below is followed:

[1.39 EE-2] [×] [9.05 EE8] [÷] [3.11 EE4] [=] [4.04 EE2] (same as 4.04×10^2)

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In multiplication and division of exponential numbers, the digital portions of the numbers are handled conventionally. For the powers of 10, in multiplication exponents are added algebraically, whereas in division the exponents are subtracted algebraically. Therefore, in the preceding example,

$$\frac{1.39 \times 10^{-2} \times 9.05 \times 10^{8}}{3.11 \times 10^{4}}$$

the digital portion is

$$\frac{1.39 \times 9.05}{3.11} = 4.04$$

and the exponential portion is,

$$\frac{10^{-2} \times 10^{8}}{10^{4}} = 10^{2} \text{ (The exponent is -2 + 8 - 4)}$$

So the answer is 4.04×10^{2}.

Example: Solve

$$\frac{7.39 \times 10^{-2} \times 4.09 \times 10^{5}}{2.22 \times 10^{4} \times 1.03 \times 10^{-3}}$$

without using exponential notation on the calculator.

Answer: Exponent of answer = $\underbrace{-2 + 5}_{\text{Algebraic addition of exponents in the numerator}} - \underbrace{(4 - 3)}_{\text{Algebraic subtraction of exponents in the denominator}} = 2$

$$\frac{7.39 \times 4.09}{2.22 \times 1.03} = 13.2$$ The answer is $13.2 \times 10^{2} = 1.32 \times 10^{3}$

Example: Solve

$$\frac{3.49 \times 10^{3}}{3.26 \times 10^{18} \times 7.47 \times 10^{-5} \times 6.18 \times 10^{-8}}$$

Answer: 2.32×10^{-4}

1.7 SIGNIFICANT FIGURES AND UNCERTAINTIES IN NUMBERS

The preceding section illustrated how to handle very large and very small numbers with *exponential notation*. This section considers **uncertainties** in numbers, taking into account the fact that numbers are known only to a certain degree of **accuracy**. The accuracy of a number is shown by how many **significant figures** or **significant digits** it contains. This can be illustrated by considering the atomic masses of elemental boron and sodium. The atomic mass of boron is given as 10.81. Written in this way, the number expressing the atomic mass of boron contains

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four significant digits—the 1, the 0, the 8, and the l. It is understood to have an uncertainty of + or - 1 in the last digit, meaning that it is really 10.81±0.01. The atomic mass of sodium is given as 22.98977, a number with seven significant digits understood to mean 22.98977±0.00001. Therefore, the atomic mass of sodium is known with more *certainty* than that of boron. The atomic masses in Table 1.1 reflect the fact that they are known with much more certainty for some elements (for example fluorine, 18.998403) than for others (for example, calcium listed with an atomic mass of 40.08).

The rules for expressing significant digits are summarized in Table 1.3. It is important to express numbers to the correct number of significant digits in chemical calculations and in the laboratory. The use of too many digits implies an accuracy in the number that does not exist and is misleading. The use of too few significant digits does not express the number to the degree of accuracy to which it is known.

Table 1.3 Rules for Use of Significant Digits

Example number	Number of significant digits	Rule
11.397	5	1. Non-zero digits in a number are always significant. The 1,1,3,9, and 7 in this number are each significant.
140.039	6	2. Zeros between non-zero digits are significant. The 1, 4, 0, 0, 3, and 9 in this number are each significant.
0.00329	3	3. Zeros on the left of the first non-zero digit are not significantbecause they are used only to locate the decimal point. Only 3, 2, and 9 in this number are significant.
70.00	4	4. Zeros to the right of a decimal point that are preceded by a significant figure are significant. All three 0s, as well as the 7, are significant.
32 000	Uncertain	5. The number of significant digits in a number with zeros to the left, but not to the right of a decimal point (1700, 110 000) may be uncertain. Such numbers should be written in exponential notation.
3.20×10^3	3	6. The number of significant digits in a number written in exponential notation is equal to the number of significant digits in the decimal portion.
Exactly 50	Unlimited	7. Some numbers, such as the amount of money that one expects to receive when cashing a check or the number of children claimed for income tax exemptions, are defined as **exact numbers** without any uncertainty.

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Exercise: Referring to Table 1.3, give the number of significant digits and the rule(s) upon which they are based for each of the following numbers:

(a) 17.000	(b) 9.5378	(c) 7.001
(d) \$50	(e) 0.00300	(f) 7400
(g) 6.207×10^{-7}	(h) 13.5269184	(i) 0.05029

Answers: (a) 5, Rule 4; (b) 5, Rule 1; (c) 4, Rule 2; (d) exact number; (e) 3, Rules 3 and 4; (f) uncertain, Rule 5; (g) 4, Rule 6; (h) 9, Rule 1; (i) 4 Rules 2 and 3

Significant Figures in Calculations

After numbers are obtained by a laboratory measurement, they are normally subjected to mathematical operations to get the desired final result. It is important that the answer have the correct number of significant figures. It should not have so few that accuracy is sacrificed or so many that an unjustified degree of accuracy is implied. The two major rules that apply, one for addition/subtraction, the other for multiplication/division, are the following:

1. In addition and subtraction, the number of digits retained to the right of the decimal point should be the same as that in the number in the calculation with the fewest such digits.

 Example: 273.591 + 1.00327 + 229.13 = 503.72427 is rounded to 503.72 because 229.13 has only two significant digits beyond the decimal.

 Example: 313.4 + 11.0785 + 229.13 = 553.6085 is rounded to 553.6 because 313.4 has only one significant digit beyond the decimal.

2. The number of significant figures in the result of multiplication/division should be the same as that in the number in the calculation having the fewest significant figures.

 Example: $\frac{3.7218 \times 4.019 \times 10^{-3}}{1.48} = 1.0106699 \times 10^{-2}$ is rounded to

 1.01×10^{-2} (3 significant figures because 1.48 has only 3 significant figures)

 Example: $\frac{5.27821 \times 10^{7} \times 7.245 \times 10^{-5}}{1.00732} = 3.7962744 \times 10^{3}$ is rounded to 3.796×10^{3} (4 significant figures because 7.245 has only 4 significant figures)

It should be noted that an exact number is treated in calculations as though it has an unlimited number of significant figures.

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Exercise: Express each of the following to the correct number of significant figures:

(a) $13.1 + 394.0000 + 8.1937$ (b) $1.57 \times 10^{-4} \times 7.198 \times 10^{-2}$

(c) $189.2003 - 13.47 - 2.563$ (d) $221.9 \times 54.2 \times 123.008$

(e) $\dfrac{603.9 \times 21.7 \times 0.039217}{87}$ (f) $\dfrac{3.1789 \times 10^{-3} \times 7.000032 \times 10^{4}}{27.130921}$

(g) $100 \times 0.7428 \times 6.82197$ (where 100 is an exact number)

Answers: (a) 415.3, (b) 1.13×10^{-5}, (c) 173.17, (d) 1.48×10^{6}, (e) 5.9, (f) 8.2019, (g) 506.7

Rounding Numbers

With an electronic calculator it is easy to obtain a long string of digits that must be rounded to the correct number of significant figures. The rules for doing this are the following:

1. If the digit to be dropped is 0, 1, 2, 3, or 4, leave the last digit unchanged

 Example: Round 4.17821 to 4 significant digits
 Answer: 4.178
 Last retained digit Digit to be dropped

2. If the digit to be dropped is 5,6,7,8 or 9, increase the last retained digit by 1

 Example: Round 4.17821 to 3 significant digits
 Answer: 4.18
 Last retained digit Digit to be dropped

Use of Three Significant Digits

It is possible to become thoroughly confused about how many significant figures to retain in an answer. In such a case it is often permissible to use 3 significant figures. Generally, this gives sufficient accuracy without doing grievous harm to the concept of significant figures.

1.8 MEASUREMENTS AND SYSTEMS OF MEASUREMENT

The development of chemistry has depended strongly upon careful measurements. Historically, measurements of the quantities of substances reacting and produced in chemical reactions have allowed the explanation of the fundamental nature of chemistry. Exact measurements continue to be of the utmost importance in chemistry and are facilitated by increasing sophisticated instrumentation. For example, atmospheric chemists can determine a small degree of stratospheric ozone depletion by measuring minute amounts of ultraviolet radiation absorbed by ozone with

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satellite-mounted instruments. Determinations of a part per trillion or less of a toxic substance in water may serve to trace the source of a hazardous pollutant. This section discusses the basic measurements commonly made in chemistry and environmental chemistry.

SI Units of Measurement

Several systems of measurement are used in chemistry and environmental chemistry. The most systematic of these is the **International System of Units**, abbreviated **SI**, a self-consistent set of units based upon the metric system recommended in 1960 by the General Conference of Weights and Measures to simplify and make more logical the many units used in the scientific and engineering community. Table 1.4 gives the seven base SI units from which all others are derived.

Multiples of Units

Quantities expressed in science often range over many orders of magnitude (many factors of 10). For example, a mole of molecular diatomic nitrogen contains 6.02×10^{23} N_2 molecules and very small particles in the atmosphere may be only about 1×10^{-6} meters in diameter. It is convenient to express very large or very small multiples by means of **prefixes** that give the number of times that the basic unit is multiplied. Each prefix has a name and an abbreviation. The ones that are used in this book, or that are most commonly encountered, are given in Table 1.5.

Metric and English Systems of Measurement

The **metric** system has long been the standard system for scientific measurement and is the one most commonly used in this book. It was the first to use multiples of 10 to designate units that differ by orders of magnitude from a basic unit. The **English** system is still employed for many measurements encountered in normal everyday activities in the United States, including some environmental engineering measurements. Bathroom scales are still calibrated in pounds, well depths may be given in feet, and quantities of liquid wastes are frequently expressed as gallons or barrels. Furthermore, English units of pounds, tons, and gallons are still commonly used in commerce, even in the chemical industry. Therefore, it is still necessary to have some familiarity with this system; conversion factors between it and metric units are given in this book.

1.9 UNITS OF MASS

Mass expresses the degree to which an object resists a change in its state of rest or motion and is proportional to the amount of matter in the object. **Weight** is the gravitational force acting upon an object and is proportional to mass. An object weighs much less in the gravitational force on the Moon's surface than on Earth, but the object's mass is the same in both places (Figure 1.7). Although mass and weight are not usually distinguished from each other in everyday activities, it is important for the science student to be aware of the differences between them.

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Table 1.4 Units of the International System of Units, SI

Physical quantity Measured	Unit name	Unit symbol	Definition
Base units			
Length	metre	m	Distance traveled by light in a vacuum in $\frac{1}{299\ 792\ 458}$ second
Mass	kilogram	kg	Mass of a platinum-iridium block located at the International Bureau of Weights and Measures at Sevres, France
Time	second	s	9 192 631 770 periods of a specified line in the microwave spectrum of the cesium-133 isotope
Temperature	kelvin	K	1/273.16 the temperature interval between absolute zero and the triple point of water at 273.16 K (0.01˚C)
Amount of substance	mole	mol	Amount of substance containing as many entities (atoms, molecules) as there are atoms in exactly 0.012 kilograms of the carbon-12 isotope
Electric current	ampere	A	—
Luminous intensity	candela	cd	—
Examples of derived units			
Force	newton	N	Force required to impart an acceleration of 1 m/s^2 to a mass of 1 kg
Energy (heat)	joule	J	Work performed by 1 newton acting over a distance of 1 meter
Pressure	pascal	Pa	Force of 1 newton acting on an area of 1 square meter

The **gram** (g) with a mass equal to 1/1000 that of the SI kilogram (see Table 1.4) is the fundamental unit of mass in the metric system. Although the gram is a convenient unit for many laboratory-scale operations, other units that are multiples of the gram are often more useful for expressing mass. The names of these are obtained by affixing the appropriate prefixes from Table 1.5 to "gram." Global burdens of atmospheric pollutants may be given in units of teragrams, each equal to 1×10^{12} grams. Significant quantities of toxic water pollutants may be measured in micrograms (1×10^{-6} grams). Large-scale industrial chemicals are marketed in units of megagrams (Mg). This quantity is also known as a metric ton, or tonne, and is somewhat larger

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(2205 lb) than the 2000-lb short ton still used in commerce in the United States. Table 1.6 summarizes some of the more commonly used metric units of mass and their relationship to some English units.

Table 1.5 Prefixes Commonly Used to Designate Multiples of Units

Prefix	Basic unit is multiplied by	Abbreviation
Mega	1 000 000 (10^6)	M
Kilo	1 000 (10^3)	k
Hecto	100 (10^2)	h
Deka	10 (10)	da
Deci	0.1 (10^{-1})	d
Centi	0.01 (10^{-2})	c
Milli	0.001 (10^{-3})	m
Micro	0.000 001 (10^{-6})	μ
Nano	0.000 000 001 (10^{-9})	n
Pico	0.000 000 000 001 (10^{-12})	p

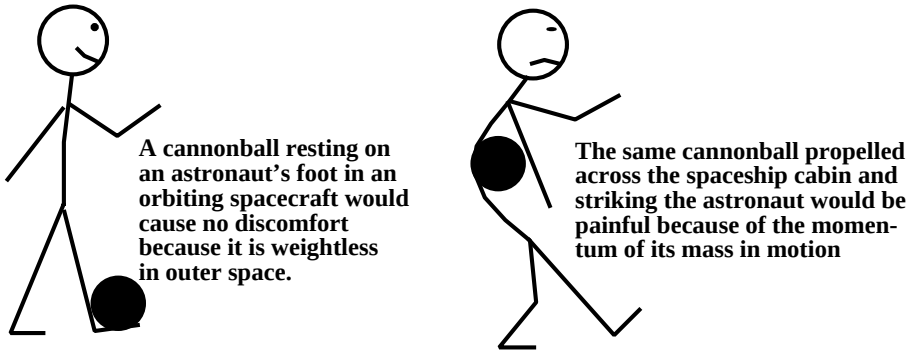


Figure 1.7 An object maintains its mass even in the weightless surroundings of outer space.

1.10 UNITS OF LENGTH

Length in the metric system is expressed in units based upon the **meter**, m (SI spelling *metre*, Table 1.4). A meter is 39.37 inches long, slightly longer than a yard. A kilometer (km) is equal to 1000 m and, like the mile, is used to measure relatively great distances. A centimeter (cm), equal to 0.01 m, is often convenient to designate lengths such as the dimensions of laboratory instruments. There are 2.540 cm per inch, and the cm is employed to express lengths that would be given in inches in the English system. The micrometer (μm) is about as long as a typical bacterial cell. The μm is also used to express wavelengths of infrared radiation by which Earth re-radiates solar energy back to outer space. The nanometer (nm), equal to 10^{-9} m, is a convenient unit for the wavelength of visible light, which ranges from 400 to 800 nm.

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Atoms are even smaller than 1 nm; their dimensions are commonly given in picometers (pm, 10^{-12} m). Table 1.7 lists common metric units of length, some examples of their use, and some related English units.

Table 1.6 Metric Units of Mass

Unit of mass	Abbreviation	Number of grams	Definition
Megagram or metric ton	Mg	10^{6}	Quantities of industrial chemicals (1 Mg = 1.102 short tons)
Kilogram	kg	10^{6}	Body weight and other quantities for which the pound has been commonly used (1 kg = 2.2046 lb)
Gram	g	1	Mass of laboratory chemicals (1 ounce = 28.35 g and 1 lb = 453.6 g)
Milligram	mg	10^{-3}	Small quantities of chemicals
Microgram	µg	10^{-6}	Quantities of toxic pollutants

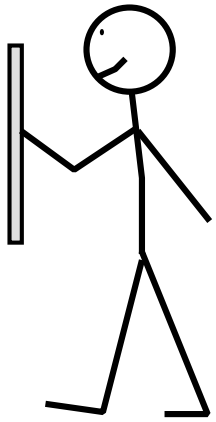


Figure 1.8 The meter stick is a common tool for measuring length.

1.11 UNITS OF VOLUME

The basic metric unit of **volume** is the **liter**, which is defined in terms of metric units of length. As shown in Figure 1.9, a liter is the volume of a decimeter cubed, that is, 1 L = 1 dm^3 (a dm is 0.1 meter, about 4 inches). A milliliter (mL) is the same volume as a centimeter cubed (cm^3 or cc), and a liter is 1000 cm^3. A kiloliter, usually designated as a cubic meter (m^3), is a common unit of measurement for the volume of air. For example, standards for human exposure to toxic substances in the workplace are frequently given in units of µg/m^3. Table 1.8 gives some common metric units of volume. The measurement of volume is one of the more frequently performed routine laboratory measurements; Figure 1.10 shows some of the more common tools for laboratory volume measurement of liquids.

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Table 1.7 Metric Units of Length

Unit of length	Abbreviation	Number of meters	Definition
Kilometer	km	10^3	Distance (1 mile = 1.609 km)
Meter	m	1	Standard metric unit of length (1 m = 1.094 yards)
Centimeter	cm	10^{-2}	Used in place of inches (1 inch = 2.54 cm)
Millimeter	mm	10^{-3}	Same order of magnitude as sizes of letters on this page
Micrometer	µm	10^{-6}	Size of typical bacteria
Nanometer	nm	10^{-9}	Measurement of light wavelength

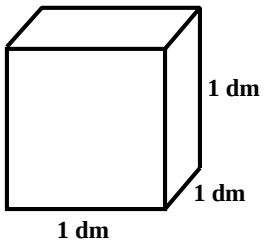


Figure 1.9 A cube that is 1 decimeter to the side has a volume of 1 liter.

Table 1.8 Metric Units of Volume

Unit of volume	Abbreviation	Number of liters	Example of use for measurement
Kiloliter or cubic meter	kL	10^3	Volumes of air in air pollution studies
Liter	L	1	Basic metric unit of volume (1 liter = 1 dm^3 = 1.057 quarts; 1 cubic foot = 28.32 L)
Milliliter	mL	10^{-3}	Equal to 1 cm^3. Convenient unit for laboratory volume measurements
Microliter	µL	10^{-6}	Used to measure very small volumes for chemical analysis

1.12 TEMPERATURE, HEAT, AND ENERGY

Temperature Scales

In chemistry, temperatures are usually expressed in metric units of **Celsius degrees**, ˚C, in which water freezes at 0˚C and boils at 100˚C. The **Fahrenheit** scale, still used for some non-scientific temperature measurements in the U.S., defines the

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freezing temperature of water at 32 degrees Fahrenheit (˚F) and boiling at 212˚F, a range of 180˚F. Therefore, each span of 100 Celsius degrees is equivalent to one of 180 Fahrenheit degrees and each ˚C is equivalent to 1.8˚F.

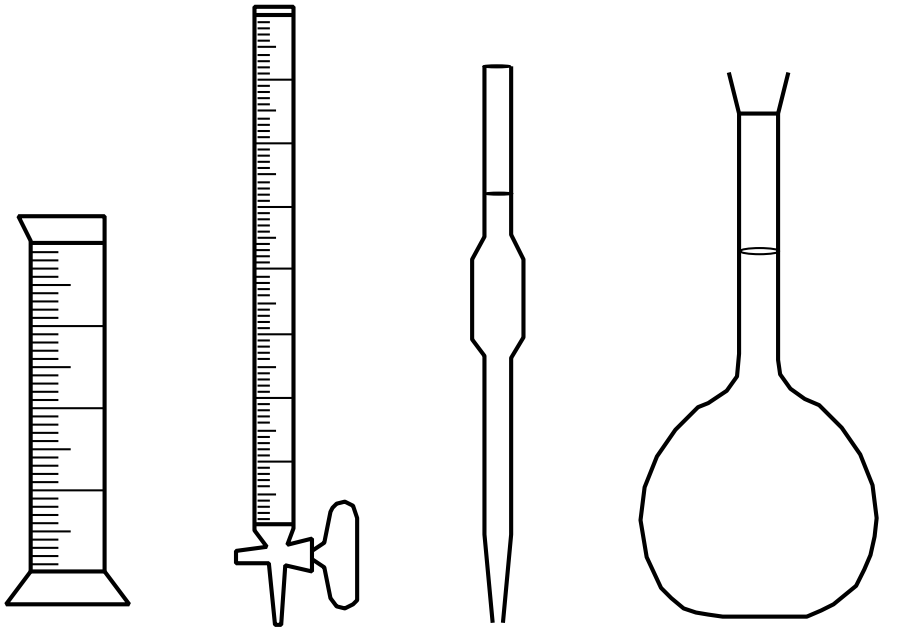


Figure 1.10 Glassware for volume measurement in the laboratory.

The most fundamental temperature scale is the **Kelvin** or **absolute** scale, for which zero is the lowest attainable temperature. A unit of temperature on this scale is equal to a Celsius degree, but it is called a **kelvin**, abbreviated K, not a degree. Kelvin temperatures are designated as K, not ˚K. The value of absolute zero on the Kelvin scale is -273.15˚C, so that the Kelvin temperature is always a number 273.15 (usually rounded to 273) higher than the Celsius temperataure. Thus water boils at 373 K and freezes at 273 K. The relationships among Kelvin, Celsius, and Fahrenheit temperatures are illustrated in Figure 1.11.

Converting from Fahrenheit to Celsius

With Figure 1.11 in mind, it is easy to convert from one temperature scale to another. Examples of how this is done are given below:

Example: What is the Celsius temperature equivalent to room temperature of 70˚F?

Answer: Step 1. Subtract 32 Fahrenheit degrees from 70 Fahrenheit degrees to get the number of Fahrenheit degrees above freezing. This is done because 0 on the Celsius scale is at the freezing point of

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water.

Step 2. Multiply the number of Fahrenheit degrees above the freezing point of water obtained above by the number of Celsius degrees per Fahrenheit degree.

$$^{\circ}C = \frac{1.00^{\circ}C}{1.80^{\circ}F} \times (70^{\circ}F - 32^{\circ}F) = \frac{1.00^{\circ}C}{1.80^{\circ}F} \times 38^{\circ}F = 21.1^{\circ}C \quad (1.12.1)$$

↑ Factor for conversion from ˚F to ˚C

↑ Number of ˚F above freezing

In working the above example it is first noted (as is obvious from Figure 1.11) that the freezing temperature of water, zero on the Celsius scale, corresponds to 32˚F on the Fahrenheit scale. So 32˚F is subtracted from 70˚F to give the number of Fahrenheit degrees by which the temperature is above the freezing point of water. The number of Fahrenheit degrees above freezing is converted to Celsius degrees above the freezing point of water by multiplying by the factor 1.00˚C/1.80˚F. The

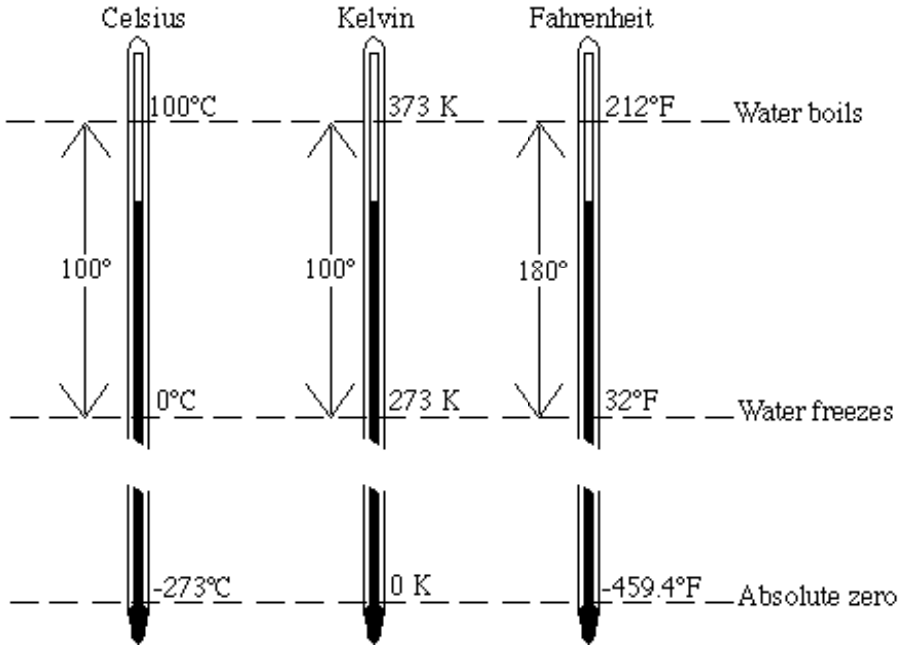


Figure 1.11 Comparison of temperature scales.

origin of this factor is readily seen by referring to Figure 1.11 and observing that there are 100˚C between the freezing and boiling temperatures of water and 180˚F over the same range. Mathematically, the equation for converting from ˚F to ˚C is simply the following:

$$^{\circ}C = \frac{1.00^{\circ}C}{1.80^{\circ}F} \times (^{\circ}F - 32) \quad (1.12.2)$$

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Example: What is the Celsius temperature corresponding to normal body temperature of 98.6˚F?

Answer: From Equation 1.12.2

$$\text{˚C} = \frac{1.00\text{˚C}}{1.80\text{˚F}} \times (98.6\text{˚F} - 32\text{˚F}) = 37.0\text{˚C} \qquad (1.12.3)$$

Example: What is the Celsius temperature corresponding to -5˚F?

Answer: From Equation 1.12.2

$$\text{˚C} = \frac{1.00\text{˚C}}{1.80\text{˚F}} \times (-5\text{˚F} - 32\text{˚F}) = \text{˚C} = -20.6\text{˚C} \qquad (1.12.4)$$

Converting from Celsius to Fahrenheit

To convert from Celsius to Fahrenheit first requires multiplying the Celsius temperature by $1.80\text{˚F}/1.00\text{˚C}$ to get the number of Fahrenheit degrees above the freezing temperature of 32˚F, then adding 32˚F.

Example: What is the Fahrenheit temperature equivalent to 10˚C?

Answer: Step 1. Multiply 10˚C by 1.80˚F/1.00˚C to get the number of Fahrenheit degrees above the freezing point of water.

Step 2. Since the freezing point of water is 32˚F, add 32˚F to the result of Step 1.

$$\text{˚F} = \frac{1.80\text{˚F}}{1.00\text{˚C}} \times \text{˚C} + 32\text{˚F} = \frac{1.80\text{˚F}}{1.00\text{˚C}} \times 10\text{˚C} + 32\text{˚F} = 50\text{˚F} \qquad (1.12.5)$$

The formula for converting ˚C to ˚F is

$$\text{˚F} = \frac{1.80\text{˚F}}{1.00\text{˚C}} \times \text{˚C} + 32\text{˚F} \qquad (1.12.6)$$

To convert from ˚C to K, add 273 to the Celsius temperature. To convert from K to ˚C, subtract 273 from K. All of the conversions discussed here can be deduced without memorizing any equations by remembering that the freezing point of water is 0˚C, 273 K, and 32˚F, whereas the boiling point is 100˚C, 373 K, and 212˚F.

Melting Point and Boiling Point

In the preceding discussion, the melting and boiling points of water were both used in defining temperature scales. These are important thermal properties of any substance. For the present, **melting temperature** may be defined as the temperature at which a substance changes from a solid to a liquid. **Boiling temperature** is defined as the temperature at which a substance changes from a liquid to a gas. More-exacting definitions of these terms, particularly boiling temperature, are given later in the book.

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Heat and Energy

As illustrated in Figure 1.12, when two objects at different temperatures are placed in contact with each other, the warmer object becomes cooler and the cooler one warmer until they reach the same temperature. This occurs because of a flow of energy between the objects. Such a flow is called **heat**.

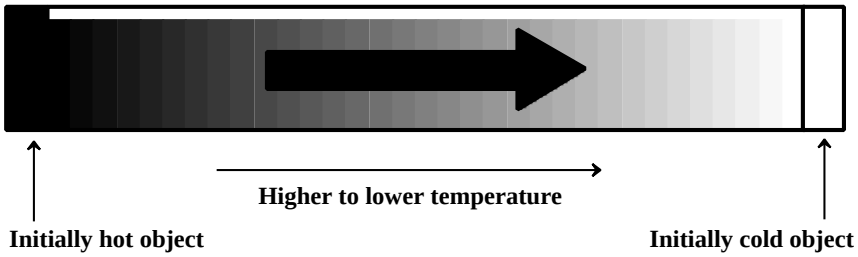


Figure 1.12 Heat energy flow from a hot to a colder object.

The SI unit of heat is the **joule** (J, see Table 1.4). The kilojoule (1 kJ = 1000 J) is a convenient unit to use to express energy values in laboratory studies. The metric unit of energy is the **calorie** (cal), equal to 4.184 J. Throughout the liquid range of water, essentially 1 calorie of heat energy is required to raise the temperature of 1 g of water by 1˚C. The "calories" most people hear about are those used to express energy values of foods and are actually kilocalories (1 kcal = 4.184 kJ).

1.13 PRESSURE

Pressure is force per unit area. The SI unit of pressure is the pascal (Pa), defined in Table 1.4. The kilopascal (1 kPa = 1000 Pa) is often a more convenient unit of pressure to use than is the pascal.

Like many other quantities, pressure has been plagued with a large number of different kinds of units. One of the more meaningful and intuitive of these is the **atmosphere** (atm), and the average pressure exerted by air at sea level is 1 atmosphere. One atmosphere is equal to 101.3 kPa or 14.7 lb/in^2. The latter means that an evacuated cube, 1 inch to the side, has a force of 14.70 lb exerted on each side due to atmospheric pressure. It is also the pressure that will hold up a column of liquid mercury metal 760 mm long, as shown in Figure 1.13. Such a device used to measure atmospheric pressure is called a **barometer**, and the mercury barometer was the first instrument used to measure pressures with a high degree of accuracy. Consequently, the practice developed of expressing pressure in units of **millimeters of mercury** (mm Hg), where 1 mm of mercury is a unit called the **torr**.

Pressure is an especially important variable with gases because the volume of a quantity of gas at a fixed temperature is inversely proportional to pressure. The temperature/pressure/volume relationships of gases (Boyle's law, Charles' law, general gas law) are discussed in Chapter 2.

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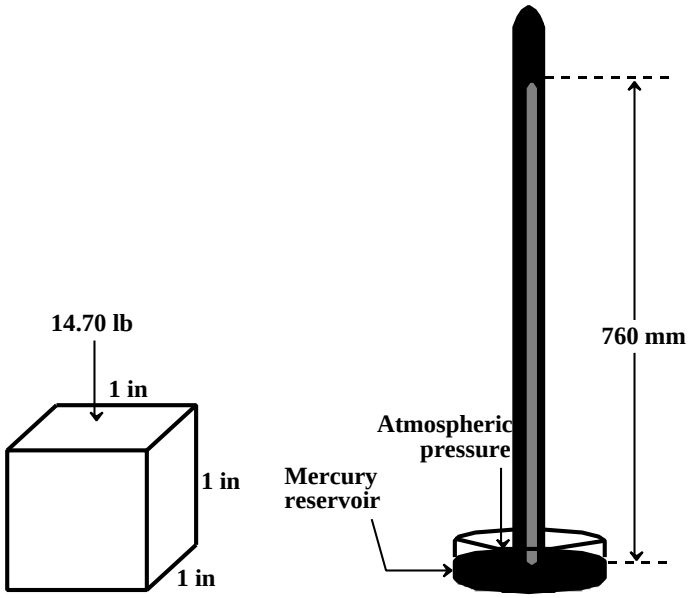


Figure 1.13 Average atmospheric pressure at sea level exerts a force of 14.7 pounds on an inch-square surface. This corresponds to a pressure sufficient to hold up a 760 mm column of mercury.

1.14 UNITS AND THEIR USE IN CALCULATIONS

Most numbers used in chemistry are accompanied by a **unit** that tells the type of quantity that the number expresses and the smallest whole portion of that quantity. For example, "36 liters" denotes that a volume is expressed and the smallest whole unit of the volume is 1 liter. The same quantity could be expressed as 360 deciliters, where the number is multiplied by 10 because the unit is only 1/10 as large.

Except in cases where the numbers express relative quantitities, such as atomic masses relative to the mass of carbon-12 or specific gravity, it is essential to include units with numbers. In addition to correctly identifying the type and magnitude of the quantity expressed, the units are carried through mathematical operations. The wrong unit in the answer shows that something has been done wrong in the calculation and it must be checked.

Unit Conversion Factors

Most chemical calculations involve calculating one type of quantity, given another, or converting from one unit of measurement to another. For example, in the chemical reaction

$$2H_2 + O_2 \rightarrow H_2O$$

someone might want to calculate the number of grams of H_2O produced when 3 g of H_2 react, or they might want to convert the number of grams of H_2 to ounces. These kinds of calculations are carried out with **unit conversion factors**. Suppose, for

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example, that the mass of a 160-lb person is to be expressed in kilograms; the person doing the calculation does not know the factor to convert from lb to kg, but does know that a 551-lb motorcycle has a mass of 250 kg. From this information the needed unit conversion factor can be derived and the calculation completed as follows:

$$\text{Mass of person in kg} = 160\ \text{lb} \times \text{unit conversion factor (problem to be solved)} \tag{1.14.1}$$

$$250\ \text{kg} = 551\ \text{lb} \quad \text{(known relationship between lb and kg)} \tag{1.14.2}$$

$$\frac{250\ \text{kg}}{551\ \text{lb}} = \frac{551\ \text{lb}}{551\ \text{lb}} = 1 \quad \text{(The unit of kg is left on top because it is the unit needed; division is by 551 lb.)} \tag{1.14.3}$$

$$\frac{0.454\ \text{kg}}{1.00\ \text{lb}} = 1 \quad \text{(The unit conversion factor in the form } 250\ \text{kg}/551\ \text{lb} \text{ could have been used, but dividing 250 by 551 gives the unit conversion factor in a more concise form.)} \tag{1.14.4}$$

$$\text{Mass of person} = 160\ \text{lb} \times \frac{0.454\ \text{kg}}{1.00\ \text{lb}} = 72.6\ \text{kg} \tag{1.14.5}$$

It is permissible to multiply 160 lb by 0.454 kg/1.00 lb because, as shown by Equation 1.14.4, this unit conversion factor has a value of exactly 1. Any quantity can be multiplied by 1 without changing the quantity itself; the only change is in the units in which it is expressed.

As another example of the use of a unit conversion factor, calculate the number of liters of gasoline required to fill a 12-gallon fuel tank, given that there are 4 gallons in a quart and that a volume of 1 liter is equal to that of 1.057 quarts. This problem can be worked by first converting gallons to quarts, then quarts to liters. For the first step, the unit conversion factor is

$$1\ \text{gal} = 4\ \text{qt} \tag{1.14.6}$$

$$\frac{1\ \text{gal}}{1\ \text{gal}} = \frac{4\ \text{qt}}{1\ \text{gal}} = 1 \quad \text{(Conversion from gallons to quarts)} \tag{1.14.7}$$

$$1.057\ \text{qt} = 1\ \text{L} \tag{1.14.8}$$

$$\frac{1.057\ \text{qt}}{1.057\ \text{qt}} = \frac{1\ \text{L}}{1.057\ \text{qt}} = 1 \quad \text{(Conversion from quarts to liters)} \tag{1.14.9}$$

Both unit conversion factors are used to calculate the capacity of the tank in liters:

$$\text{Tank capacity} = 12\ \text{gal} \times \frac{4\ \text{qt}}{1\ \text{gal}} \times \frac{1\ \text{L}}{1.057\ \text{qt}} = 45.4\ \text{L} \tag{1.14.10}$$

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Cancellation of Units

The preceding examples show that units are canceled in mathematical operations, just as numbers may be. When the same unit appears both above and below the line in a mathematical operation, the units cancel. An example of such an operation is shown for lb in the following:

$$160 \text{ lb} \times \frac{0.454 \text{ kg}}{1.00 \text{ lb}}$$

The unit of lb simply cancels, leaving kg as the unit remaining.

Calculation of Some Unit Conversion Factors

Several values of units are given that enable conversion between metric and English units in Table 1.6 (mass), Table 1.7 (length), and Table 1.8 (volume). For example, Table 1.6 states that a megagram (Mg, metric ton) is equal to 1.102 short tons (T). By using this equality to give the correct unit conversion factors, it is easy to calculate the number of metric tons in a given number of short tons of material or vice versa. To do this, first write the known equality given that a megagram is equal to 1.102 short tons:

$$1 \text{ Mg} = 1.102 \text{ T} \tag{1.14.11}$$

If the number of Mg is to be calculated given a mass in T, the unit conversion factor needed is

$$\frac{1 \text{ Mg}}{1.102 \text{ T}} = \frac{1.102 \text{ T}}{1.102 \text{ T}} = 1 \tag{1.14.12}$$

leaving Mg on top. Suppose, for example, that the problem is to calculate the mass in Mg of a 3521 T shipment of industrial soda ash. The calculation involves simply multiplying the known mass in T times the unit conversion factor required to convert to Mg:

$$3521 \text{ T} \times \frac{1 \text{ Mg}}{1.102 \text{ T}} = 3195 \text{ Mg} \tag{1.14.12}$$

If the problem had been to calculate the number of T in 789 Mg of copper ore, the following steps would be followed:

$$1.102 \text{ T} = 1 \text{ Mg}, \qquad \frac{1.102 \text{ T}}{1 \text{ Mg}} = \frac{1 \text{ Mg}}{1 \text{ Mg}} = 1, \tag{1.14.13}$$

$$789 \text{ Mg} \times \frac{1.102 \text{ T}}{1 \text{ Mg}} = 869 \text{ T copper ore} \tag{1.14.14}$$

Table 1.9 gives some unit conversion factors calculated from the information given in Tables 1.6–1.8 and in preceding parts of this chapter. Note that in each case, two unit conversion factors are calculated; the one that is used depends upon the units that are required for the answer.

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Table 1.9 Examples of Some Unit Conversion Factors

Equality	Conversion factors	
1 kg = 2.2046 lb	$\frac{1\text{ kg}}{2.2046\text{ lb}} = 1$	$\frac{2.2046\text{ lb}}{1\text{ kg}} = 1$
1 oz = 28.35 g	$\frac{1\text{ oz}}{28.35\text{ g}} = 1$	$\frac{28.35\text{ g}}{1\text{ oz}} = 1$
1 mi = 1.609 km	$\frac{1\text{ mi}}{1.609\text{ km}} = 1$	$\frac{1.609\text{ km}}{1\text{ mi}} = 1$
1 in = 2.54 cm	$\frac{1\text{ in}}{2.54\text{ cm}} = 1$	$\frac{2.54\text{ cm}}{1\text{ in}} = 1$
1 L = 1.057 qt	$\frac{1\text{ L}}{1.057\text{ qt}} = 1$	$\frac{1.057\text{ qt}}{1\text{ L}} = 1$
1 cal = 4.184 J	$\frac{1\text{ cal}}{4.184\text{ J}} = 1$	$\frac{4.184\text{ J}}{1\text{ cal}} = 1$
1 atm = 101.4 kPa	$\frac{1\text{ atm}}{101.4\text{ kPa}} = 1$	$\frac{101.4\text{ kPa}}{1\text{ atm}} = 1$

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Chemistry is defined as [1] _____. Environmental chemistry is [2] _____ _____. Toxicological chemistry is defined as [3] _____ _____. All matter is composed of only about a hundred fundamental kinds of matter called [4] , each composed of very small entities called [5] _____ _____. The three major subatomic particles and their charges are [6] _____ _____. Of these, the two that have relatively high masses are contained in the [7] _____ of the atom. The subatomic particles with a relatively low mass are contained in [8] _____ _____ in the atom. The number of protons in the nucleus of each atom of an element is the [9] _____ of the element. Each element is represented by an abbreviation called a [10] _____. In addition to atomic number, name, and chemical symbol, each element has a characteristic [11] _____. Atoms of most elements consist of two or more isotopes that have different [12] _____ _____. An arrangement of the elements in a manner

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that reflects their recurring behavior with increasing atomic number is the [13] _____ _____ in which elements with similar chemical properties are called [14] _____ and are contained in [15] _____ _____ in the periodic table. Instead of existing as atoms, elemental hydrogen consists of [16] _____, each consisting of [17] _____ _____ linked by a [18]_____. Water is not an element, but is a [19]_____, for which the [20] _____ _____ is H_2O. Species consisting of electrically charged atoms or groups of atoms are called [21]_____. Those with positive charges are called [22]_____ and those with negative charges are [23] _____. Compounds made of these kinds of entities are held together by [24] _____ bonds. The average mass of all molecules of a compound is its [25]_____, which is calculated by [26]_____ _____. [27]_____ occur when substances are changed to other substances through the breaking and formation of chemical bonds and are written as [28] _____. To be correct, these must be [29]_____. In them, the arrow is read as [30]_____ and separates the [31]_____ from the [32]_____. Very large or small numbers are conveniently expressed in [33]_____, which is the product of a [34]_____ _____ with a value equal to or greater than [35]_____ and less than [36] _____ multiplied times a [37]_____. In such a notation, 3,790,000 is expressed as [38]_____ and 0.000 000 057 is expressed as [39]_____. The accuracy of a number is shown by how many [40] it contains. Non-zero digits in a number are always [41]_____. Zeros between non-zero digits are [42]_____ _____. Zeros on the left of the first non-zero digit are [43]_____. Zeros to the right of a decimal point that are preceded by a significant figure are [44] _____. The number of significant digits in a number written in exponential notation is equal to [45]_____ _____. Some numbers, such as the amount of money that one expects to receive when cashing a check are defined as [46]_____. In addition and subtraction, the number of digits retained to the right of the decimal point should be [47]_____ _____. The number of significant figures in the result of multiplication/division should be [48] . In rounding numbers, if the digit to be dropped is 0, 1, 2, 3, or 4, [49]_____ _____, whereas if the digit to be dropped is 5,6,7,8 or 9,[50]_____. A self-consistent set of units based upon the metric system is the [51]_____ _____. [52]_____ is proportional to the amount of matter in an object, the metric unit for which is the [53]_____. Length in the metric system is expressed in units based upon the [54]_____. The basic metric unit of volume is the [55]_____. In ˚C, ˚F, and K, respectively, water freezes at [56] and boils at [57]_____. Boiling temperature is defined as [58] _____. Energy that flows from a warmer to a colder object is called [59]_____,

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commonly expressed in units of [60]_____ or [61]_____. [62]_____ is force per unit area, some of the common units for which are [63]_____ _____. A unit after a number tells the [64]_____ that the number expresses and the smallest [65]_____. The quantity $0.454\ kg/1\ lb$ is an example of [66]_____.

Answers to Chapter Summary

1. the science of matter
2. that branch of chemistry that deals with the origins, transport, reactions, effects, and fates of chemical species in the water, air, earth, and living environments and the effects of human activities thereon
3. the chemistry of toxic substances with emphasis upon their interaction with biologic tissue and living systems
4. elements
5. atoms
6. positively charged protons, negatively charged electrons, and uncharged (neutral) neutrons
7. nucleus
8. a cloud of negative charge
9. atomic number
10. chemical symbol
11. atomic mass
12. numbers of neutrons in their nuclei
13. periodic table
14. groups of elements
15. vertical columns
16. molecules
17. 2 H atoms
18. chemical bond
19. chemical compound
20. chemical formula
21. ions
22. cations
23. anions
24. ionic
25. molecular mass
26. multiplying the atomic mass of each element by the relative number of atoms of the element, then adding all the values obtained for each element in the compound
27. Chemical reactions
28. chemical equations
29. balanced
30. yields
31. reactants
32. products

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33. exponential notation
34. digital number
35. exactly 1
36. exactly 10
37. power of 10
38. 3.79×10^{6}
39. 5.7×10^{-8}
40. significant figures or significant digits
41. significant
42. significant
43. not significant
44. significant
45. the number of significant digits in the decimal portion
46. exact numbers
47. the same as that in the number in the calculation with the fewest such digits
48. the same as that in the number in the calculation having the fewest significant figures
49. leave the last digit retained unchanged
50. increase the last retained digit by 1
51. International System of Units, SI
52. Mass
53. gram
54. meter
55. liter
56. 0˚C, 32˚F, and 273 K
57. 100˚C, 212˚F, and 373 K
58. the temperature at which a substance changes from a liquid to a gas
59. heat
60. joules
61. calories
62. Pressure
63. atmosphere, torr, mm Hg, lb/in^2
64. type of quantity
65. whole portion of that quantity
66. a unit conversion factor

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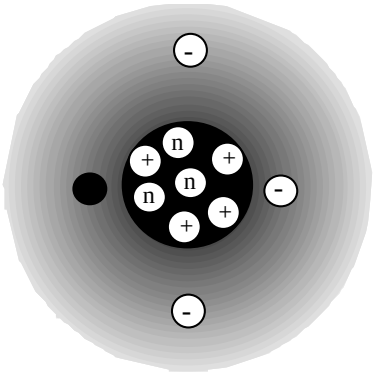
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QUESTIONS AND PROBLEMS

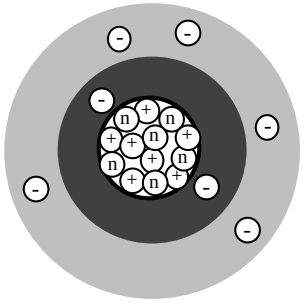
Section 1.3. The Building Blocks of Matter

1. Consider the following atom:

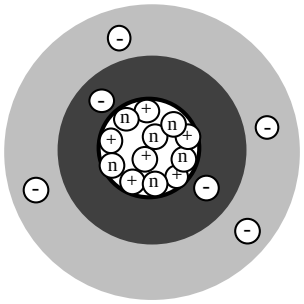


How many electrons, protons, and neutrons does it have? What is its atomic number? Give the name and chemical symbol of the element of which it is composed.

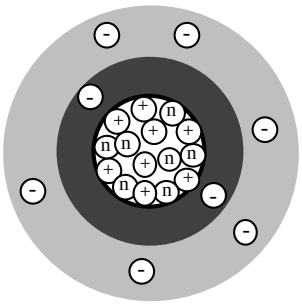
2. Give the numbers of electrons, protons, and neutrons in each of the atoms represented below. Give the atomic numbers, names, and chemical symbols of each of the elements represented.



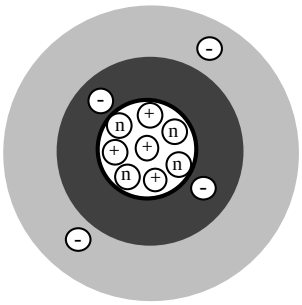
A



B



C



D

3. What distinguishes a radioactive isotope from a “normal” stable isotope?

4. Why is the periodic table so named?

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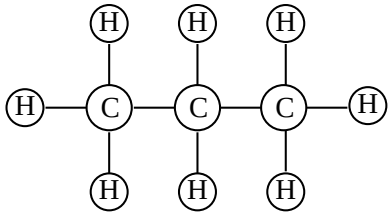
Section 1.4. Chemical Bonds and Compounds

5. Match the following:

A. O_2	1. Element consisting of individual atoms
B. NH_3	2. Element consisting of chemically bonded atoms
C. Ar	3. Ionic compound
D. NaCl	4. Covalently bound compound

6. After examining Figure 1.6, consider what might happen when an atom of sodium (Na), atomic number 11, loses an electron to an atom of fluorine, (F), atomic number 9. What kinds of particles are formed by this transfer of a negatively charged electron? Is a chemical compound formed? What is it called?

7. Give the chemical formula and molecular mass of the molecule represented below:



8. Calculate the molecular masses of (a) C_2H_2, (b) N_2H_4, (c) Na_2O, (d) O_3 (ozone), (e) PH_3, (f) CO_2, (g) C_3H_9O.

9. Match the following:

A. Periodic table	1. Has groups
B. Elemental hydrogen	2. Consists of ions
C. Water H_2O	3. Consists of covalently bonded (shared electrons) molecule containing two different elements
D. Magnesium oxide, MgO	4. Consists of diatomic, covalently bonded molecules

Section 1.5. Chemical Reactions and Equations

10. Is the equation, $H_2 + O_2 \rightarrow H_2O$, a balanced chemical equation? Explain. Point out the reactants and products in the equation.

Section 1.6. Numbers in Chemistry: Exponential Notation

11. Write each of the following in exponential form to three significant figures: (a) 321,000, (b) 0.000 005 29, (c) 5170, (d) 000 000 000 000 784, (e) 86,300,000,000,000.

12. Write each of the following in decimal form: (a) 7.49×10^{3}, (b) 9.6×10^{-5}, (c) 1.16×10^{21}, (d) 4.47×10^{-17}, (e) 2.93×10^{13}.

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13. Without using a calculator, calculate the sum $4.13 \times 10^3 + 8.76 \times 10^2 + 1.22 \times 10^4$ expressed to three significant figures in the correct exponential notation.

14. Without using a calculator, calculate the sum $4.13 \times 10^{-4} + 8.76 \times 10^{-3} + 1.22 \times 10^{-2}$ expressed to three significant figures in the correct exponential notation.

15. Without using a calculator for the exponential portions, calculate $1.39 \times 10^{-2} \times 9.05 \times 10^8 \times 3.11 \times 10^4$.

16. Without using a calculator for the exponential portions, calculate

$$\frac{9.05 \times 10^{-6} \times 3.19 \times 10^3}{4.02 \times 10^5 \times 1.93 \times 10^{-7}}$$

Section 1.7. Significant Figures and Uncertainties in Numbers

17. Match the following numbers, with the significant figures for each given in parentheses with the rule for assigning significant figures that applies to each:

A. 0.00027(2)	1. Non-zero digits in a number are always significant.
B. 7.28139(6)	2. Zeros between non-zero digits are significant.
C. 7.4×10^3(2)	3. Zeros on the left of the first non-zero digit are not significant.
D. \$50(infinite)	4. Zeros to the right of a decimal point that are preceded by a significant figure are significant.
E. 81.000(5)	5. The number of significant digits in a number written in exponential notation is equal to the number of significant digits in the decimal portion.
F. 40.007(5)	6. Some numbers are defined as exact numbers without any uncertainty.

18. Using the appropriate rules, round each of the following to the correct number of significant digits: (a) 923.527 + 3.02891 + 729.29, (b) 273.591 + 12.72489 + 0.1324, (c) 473+ 9.3827 + 349.17, (d) 693.59102 + 9.00327 + 229.461853.

19. Using the appropriate rules, round each of the following to the correct number of significant digits: (a) $3.52 \times 8.02891 \times 729$, (b) $4.52 \times 10^3 \times 8.021 \times 0.5779$,

(c) $\frac{7.7218 \times 10^7 \times 4.019 \times 10^{-3}}{1.48 \times 10^{-5}}$, (d) $\frac{7.8 \times 6.028 \times 10^{-3}}{4.183 \times 10^{-5} \times 2.19 \times 10^5}$

20. Round each of the following properly: (a) 7.32987 to 3 places, (b) 1.193528 to 4 places, (c) 7.1382×10^3 to 2 places (d) 9.04557×10^{-17} to 4 places, (e) 71235.801 to 3 places, (f) 5.8092355 to 3 places.

21. How many significant digits does each of the following numbers have?

A. 7.8231 B. 7.63×10^5

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C. 0.004 D. 20.071

Section 1.8. Measurements and Systems of Measurement

22. Match the following numbers, for each of which the significant figures are given in parentheses, with the rule for assigning significant figures that applies to each:

A. Mole	1. 1/273.16 the temperature interval between absolute zero and the triple point of water at 273.16 K (0.01˚C)
B. Metre	
C. Gram	2. Metric unit of volume
D. Kelvin	3. SI unit for amount of substance
E. Liter	4. Metric unit of mass
	5. Distance traveled by light in a vacuum in $\frac{1}{299\ 792\ 458}$ second

23. Match the abbreviations below with the numbers they represent:

A. Centi	D. Micro	1. $\times 10^{-3}$	4. $\times 10$
B. Kilo	E. Milli	2. $\times 10^{-6}$	5. $\times 0.01$
C. Deka		3. $\times 1000$	

Section 1.9. Units of Mass.

24. Denote each of the following as characteristic of mass (*m*) or characteristic of weight (*w*):

A. Varies with gravity

B. Degree to which an object resists a change in its state of rest or motion

C. Direct measure of the amount of matter in the object

D. Different on the Moon's surface than on Earth

25. Match the following units on the left, below, with the quantity they are most likely to be used to express:

A. Mg	1. Quantities of toxic pollutants
B. µg	2. Quantities of large-scale industrial chemicals
C. kg	3. Quantities of laboratory chemicals
D. g	4. Global burdens of atmospheric pollutants
E. Teragrams	5. Body mass

26. Calculate (a) the number of grams in 1.56 pounds, (b) the number of kilograms in a 2000-pound ton, (c) the number of g in 2.14 kg, (d) the number of atmospheric dust particles, each weighing an average of 2.56 µg, to make up an ounce of dust particles.

Section 1.10. Units of Length

27. Distinguish between a meter and a metre.

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28. How tall is a 6-foot person in cm?

29. Estimate approximately how many bacterial cells would have to be laid end-to-end to reach an inch.

30. Match the following units on the left, below, with the quantity they are most likely to be used to measure:

A. km	1. Distance between this line and the line directly below
B. m	2. Distance run by an athlete in 5 seconds
C. Nanometer	3. Distance traveled by an automobile in 1 hour
D. Centimeter	4. Dimensions of this book
E. mm	5. Wavelength of visible light

Section 1.11. Units of Volume

31. Explain how metric units of volume can be defined in terms of length.

32. Recalling the appropriate formula from elementary geometry, what is the volume in liters of a round tank with a radius of 39.0 cm and a depth of 15.0 cm?

33. Consider gasoline at a price of $1.45 per gallon. What is its equivalent price in dollars per liter ($/L)?

34. Match the following units on the left, below, with the quantity they are most likely to be used to measure:

A. Milliliter	1. Volume of milk
B. Kiloliter	2. Volume of a laboratory chemical
C. Microliter	3. Volume of air in air pollution studies
D. Liter	4. Volume of chemical reagent in a syringe for chemical analysis

35. Give the volume in liters of cubes that are (A) 12 cm, (B) 14 cm, and (C) 17.2 cm to the side.

Section 1.12. Temperature, Heat, and Energy

36. Convert each of the following Fahrenheit temperatures to Celsius and Kelvin: (a) 237˚F, (b) 105˚F, (c) 17˚F, (d) 2˚F, (e) -32˚F, (f) -5˚F, (g) 31.2˚F.

37. Convert each of the following Celsius temperatures to Fahrenheit: (a) 237˚C, (b) 75˚C, (c) 17˚C, (d) 100˚C, (e) -32˚C, (f) -40˚C, (g) -11˚C.

38. Convert each of the following Celsius temperatures to Kelvin: (a) 237˚C, (b) 75˚C, (c) 48˚C, (d) 100˚C, (e) -0˚C, (f) -40˚C, (g) -200˚C.

39. Calculate the value of temperature in ˚F that is numerically equal to the temperature in ˚C.

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40. The number 1.8 can be used in making conversions between Fahrenheit and Celsius temperatures. Explain how it is used and where it comes from in this application.

41. Calculate how many calories there are in 1 joule.

1.13. Pressure

42. Match each of the following pertaining to units of pressure:

A. pascal	1. Based on a column of liquid
B. atm	2. Takes 14.7 to equal 1 atm
C. mm Hg	3. SI unit
D. lb/in^2	4. Essentially 1 for air at sea level.

43. Try to explain why pressure is a more important variable for gases than for liquids.

44. The pressure in a typical automobile tire is supposed to be 35 lb/in^2 (above normal atmospheric pressure). Calculate the equivalent pressure in (a) pascal, (b) atm, and (c) torr.

45. Knowing that there are 12 inches per foot, calculate the normal pressure of the atmosphere in lb/ft^2.

46. Atmospheric pressure readings on weather reports in the U.S. used to be given as 29–30 "inches." Speculate on what such a reading might mean.

1.14. Units and their Use in Calculations

47. Using unit conversion factors, calculate the following:

 (a) A pressure in inches of mercury eqivalent to 1 atm pressure

 (b) The mass in metric tons of 760,000 tons of contaminated soil

 (c) The number of cubic meters in a cubic mile of atmospheric air

 (d) The cost of 100 liters of gasoline priced at $1.33/gallon.

 (e) The number of kilograms of cheese in 200 ounces of this food

 (f) The pressure in kPa equivalent to 5.00 atm pressure

48. An analyst reported some titration data as "34.52 mL." What two things are stated by this expression?

49. Why is it not wrong to give the atomic mass of aluminum as 26.98, even though a unit is not specified for the mass?

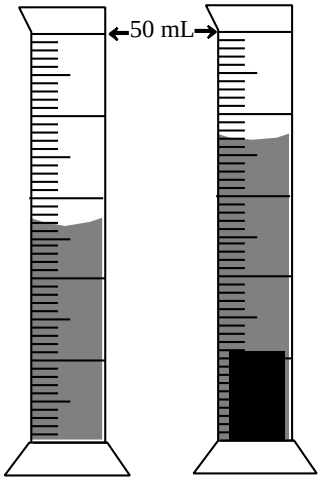
50. Explain what is meant by a unit conversion factor. How is such a factor used? Why may quantities be multiplied by a proper unit conversion factor without concern about changing the magnitude of the quantity?

51. Consider only the following information: *An object with a mass of 1 kg also has a mass of 2.2046 lb. A pound contains 16 ounces. A piece of chalk 2 inches*

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long is also 5.08 cm long. There are 36 inches in 1 yard. A 1-liter volumetric flask contains 1.057 quarts. A cubic centimeter is the same volume as a milliliter. From this information show how to calculate unit conversion factors to convert the following: (a) From yards to meters, (b) from ounces to grams, (c) from quarts to deciliters, (d) from cubic inches to cubic centimeters.

52. A quantity of colored water was poured into a 50-mL graduated cylinder, raising it to the level shown on the left in the figure. Next, an object with a mass of 25.2 g was placed in the water, raising the level to that shown on the right. What was the density of the object in g/mL?



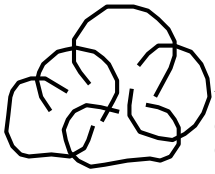
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Manahan, Stanley E. "MATTER AND PROPERTIES OF MATTER"
Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

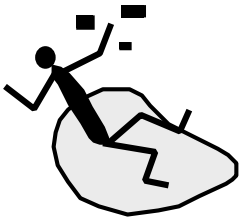
2 MATTER AND PROPERTIES OF MATTER

2.1 WHAT IS MATTER?

In Chapter 1, chemistry was defined as the science of **matter**, *anything that has mass and occupies space.* This chapter deals specifically with matter—what it is, how it acts, what its properties are. Most of this book is concerned with chemical processes—those in which chemical bonds are broken and formed to produce different substances—and the *chemical properties* that they define. However, before going into chemical phenomena in any detail, it is helpful to consider matter in its bulk form, aside from its chemical behavior. Non-chemical aspects include physical



Warm, moist air tends to rise, causing cloud formation and influencing atmospheric chemistry



A layer of ice—matter in the solid state—can be hard on pedestrians



A small amount of matter consumed in a nuclear reaction can release an awesome amount of energy

Figure 2.1 Different kinds of matter have a vast variety of properties that determine what matter does and how it is used.

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state—whether a substance is a solid, liquid, or gas—color, hardness, extent to which matter dissolves in water, melting temperature, and boiling temperature. These kinds of *physical properties* are essential in describing the nature of matter and the chemical changes that it undergoes. They are also essential in understanding and describing its environmental chemical and biological behavior. For example, as discussed in Chapter 11, the temperature-density relationships of water result in stratification of bodies of water such that much different chemical and biochemical processes occur at different depths in a pond, lake, or reservoir. An analogous stratification of the atmosphere profoundly influences atmospheric chemistry.

2.2 CLASSIFICATION OF MATTER

Matter exists in the form of either *elements* or *compounds* (see Sections 1.3 and 1.4, respectively). Recall that compounds consist of atoms of two or more elements bonded together. Chemical changes in which chemical bonds are broken or formed are involved when a compound is produced from two or more elements or from other compounds, or when one or more elements are isolated from a compound. These kinds of changes, which are illustrated by the examples in Table 2.1, profoundly affect the properties of matter. For example, the first reaction in the table shows that sulfur (S), a yellow, crumbly solid, reacts with oxygen, a colorless, odorless gas that is essential for life, to produce sulfur dioxide, a toxic gas with a choking odor. In the second reaction in Table 2.1, the hydrogen atoms in methane, CH_4, a highly flammable, light gas, are replaced by chlorine atoms to produce carbon tetrachloride, CCl_4, a dense liquid so nonflammable that it has been used as a fire extinguisher.

Table 2.1 Chemical Processes Involving Elements and Compounds

Type of Process	Chemical reaction
Two elements combining to form a chemical compound, sulfur plus oxygen yields sulfur dioxide	$S + O_2 \rightarrow SO_2$
A compound reacting with an element to form two different compounds, methane plus chlorine yields carbon tetrachloride plus hydrogen chloride	$CH_4 + 4Cl_2 \rightarrow CCl_4 + 4HCl$
Two compounds reacting to form a different compound, calcium oxide plus water yields calcium hydroxide	$CaO + H_2O \rightarrow Ca(OH)_2$
A compound plus an element reacting to produce another compound and another pure element, iron oxide plus carbon yields carbon monoxide plus elemental iron (Fe)	$Fe_2O_3 + 3C \rightarrow 3CO + 2Fe$
A compound breaking down to its constituent elements, passing an electrical current through water yields hydrogen and oxygen	$2H_2O \rightarrow 2H_2 + O_2$

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Some General Types of Matter

In discussing matter, some general terms are employed that are encountered frequently enough that they should be mentioned here. More-exact definitions are given later in the text.

Elements are divided between metals and nonmetals; several elements with properties of both metals and nonmetals are called **metalloids**. **Metals** are elements that are generally solid, shiny in appearance, electrically conducting, and malleable—that is, they can be pounded into flat sheets without disintegrating. Examples of metals are iron, copper, and silver. Most metallic objects that are commonly encountered are not composed of just one kind of elemental metal, but are alloys consisting of homogeneous mixtures of two or more metals. **Nonmetals** often have a dull appearance and are not at all malleable. In contrast to metals, all of which except mercury exist as solids at room temperatures, nonmetals frequently occur as gases or liquids. Colorless oxygen gas, green chlorine gas (transported and stored as a liquid under pressure), and brown bromine liquid are common nonmetals. In a very general sense, we tend to regard as nonmetals substances that actually contain metal in a chemically combined form. One would classify table salt, sodium chloride, as a nonmetal even though it contains chemically bound sodium metal.

Another general classification of matter is in the categories of inorganic and organic substances. **Organic substances** consist of virtually all compounds that contain carbon, including substances made by life processes (wood, flesh, cotton, wool), petroleum, natural gas (methane), solvents (dry cleaning fluids), synthetic fibers, and plastics. All of the rest of the chemical kingdom is composed of **inorganic substances** made up of virtually all substances that do not contain carbon. These include metals, rocks, table salt, water, sand, and concrete.

Mixtures and Pure Substances

Matter consisting of only one compound or of only one form of an element is a **pure substance**; all other matter is a **mixture** of two or more substances. The compound water with nothing dissolved in it is a pure substance. Highly purified helium gas is an elemental pure substance. The composition of a pure substance is defined and constant and its properties are always the same under specified conditions. Therefore, pure water at -1˚C is always a solid (ice), whereas a mixture of water and salt might be either a liquid or a solid at that temperature, depending upon the amount of salt dissolved in the water. Air is a mixture of elemental gases and compounds, predominantly nitrogen, oxygen, argon, carbon dioxide, and water vapor. Drinking water is a mixture containing calcium ion (Ca^{2+}, see ions in Section 1.4), hydrogen carbonate ion, (bicarbonate, HCO_3^-), nitrogen gas, carbon dioxide gas, and other substances dissolved in the water. Mixtures can be separated into their constituent pure substances by **physical processes**. Liquified air is distilled to isolate pure oxygen (used in welding, industrial processes, for some specialized wastewater treatment processes, and for breathing by people with emphysema), liquid nitrogen (used for quick-freezing frozen foods), and argon (used in specialized types of welding because of its chemically non-reactive nature).

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Homogeneous and Heterogeneous Mixtures

A **heterogeneous mixture** is one that is not uniform throughout and possesses readily distinguishable constituents (matter in different phases, see Section 2.5) that can be isolated by means as simple as mechanical separation. Concrete (see Figure 2.2) is such a mixture; individual grains of sand and pieces of gravel can be separated from concrete with a pick or other tool. **Homogeneous mixtures** are uniform throughout; to observe different constituents would require going down to molecular levels. Homogeneous mixtures may have varying compositions and consist of two or more chemically distinct consituents, so they are not pure substances. Air, well filtered to remove particles of dust, pollen, or smoke, is a homogeneous mixture. Homogeneous mixtures are also called **solutions**, a term that is usually applied to mixtures composed of gases, solids, and other liquids dissolved in a liquid. A hazardous-waste leachate is a solution containing—in addition to water—contaminants such as dissolved acids, iron, heavy metals, and toxic organic compounds. Whereas mechanical means, including centrifugation and filtration, can be used to separate the solids from the liquids in a heterogeneous mixture of solids and liquids, the isolation of components of homogeneous mixtures requires processes such as distillation and freezing.

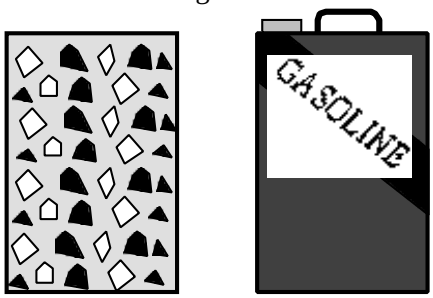


Figure 2.2. Concrete (left) is a heterogeneous mixture with readily visible grains of sand, pieces of gravel, and cement dust. Gasoline is a homogeneous mixture consisting of a solution of petroleum hydrocarbon liquids, dye, and additives such as ethyl alcohol to improve its fuel qualities.

Summary of the Classification of Matter

As discussed above, all matter consists of compounds or elements. These may exist as pure substances or mixtures; the latter may be either homogeneous or heterogeneous. These relationships are summarized in Figure 2.3.

2.3 QUANTITY OF MATTER: THE MOLE

One of the most fundamental characteristics of a specific body of matter is the quantity of it. In discussing the quantitative chemical characteristics of matter it is essential to have a way of expressing quantity in a way that is proportional to the number of individual entities of the substance—that is, atoms, molecules, or ions—in numbers that are readily related to the properties of the atoms or molecules of the substance. The simplest way to do this would be as individual atoms, molecules, or ions, but for laboratory quantities, these would number the order of 10^{23}, far too large

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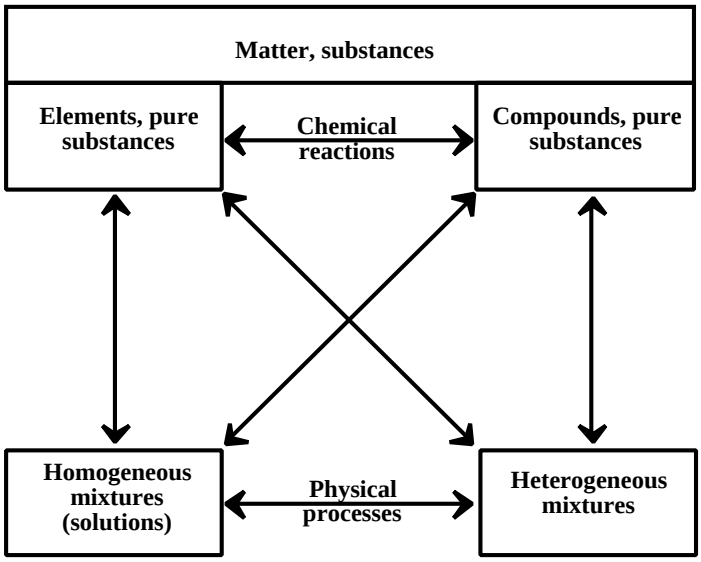


Figure 2.3 Classification of matter

to be used routinely in expressing quantities of matter. Instead, such quantities are readily expressed as moles of substance. A mole is defined in terms of specific entities, such as atoms of Ar, molecules of H_2O, or Na^+ and Cl^- ions, each pair of which composes a "molecule" of NaCl. A **mole** is defined as *the quantity of substance that contains the same number of specified entities as there are atoms of C in exactly 0.012 kg (12 g) of carbon-12*. It is easier to specify the quantity of a substance equivalent to its number of moles than it is to define the mole. To do so, simply state the atomic mass (of an element) or the molecular mass (of a compound) and affix "mole" to it as shown by the examples below:

- *A mole of argon, which always exists as individual Ar atoms:* The atomic mass of Ar is 40.0. Therefore exactly one mole of Ar is 40.0 grams of argon.
- *A mole of molecular elemental hydrogen, H_2:* The atomic mass of H is 1.0, the molecular mass of H_2 is, therefore, 2.0, and a mole of H_2 is 2.0 g of H_2.
- *A mole of methane, CH_4:* The atomic mass of H is 1.0 and that of C is 12.0, so the molecular mass of CH_4 is 16.0. Therefore a mole of methane has a mass of 16.0 g.

The Mole and Avogadro's Number

In Section 1.6, Avogadro's number was mentioned as an example of a huge number, 6.02×10^{23}. **Avogadro's number** *is the number of specified entities in a mole of substance.* The "specified entities" may consist of atoms or molecules or they may be groups of ions making up the smallest possible unit of an ionic

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compound, such as 2 Na^+ ions and one S^{2-} ion in Na_2S. (It is not really correct to refer to Na_2S as a molecule because the compound consists of ions arranged in a crystalline structure such that there are 2 Na^+ ions for each S^{2-} ion.) A general term that covers all these possibilities is the **formula unit**. The average mass of a formula unit is called the **formula mass**. Examples of the terms defined in this section are given in Table 2.2.

2.4 PHYSICAL PROPERTIES OF MATTER

Physical properties of matter are those that can be measured without altering the chemical composition of the matter. A typical physical property is color, which can be observed without changing matter at all. Malleability of metals, the degree to which they can be pounded into thin sheets, certainly alters the shape of an object but does not change it chemically. On the other hand, observation of a *chemical property*, such as whether sugar burns when ignited in air, potentially involves a complete change in the chemical composition of the substance tested.

Physical properties are important in describing and identifying particular kinds matter. For example, if a substance is liquid at room temperature, has a lustrous metallic color, conducts electricity well, and has a very high density (mass per unit volume) of 13.6 g/cm^3, it is doubtless elemental mercury metal. Physical properties are very useful in assessing the hazards and predicting the fates of environmental pollutants. An organic substance that readily forms a vapor (volatile organic compound) will tend to enter the atmosphere or to pose an inhalation hazard. A brightly colored water soluble pollutant may cause deterioration of water quality by adding water "color." Much of the health hazard of asbestos is its tendency to form extremely small-diameter fibers that are readily carried far into the lungs and that can puncture individual cells.

Several important physical properties of matter are discussed in this section. The most commonly considered of these are density, color, and solubility. Thermal properties are addressed separately in Section 2.9.

Density

Density (d) is defined as mass per unit volume and is expressed by the formula

$$d = \frac{\text{mass}}{\text{volume}} \tag{2.4.1}$$

Density is useful for identifying and characterizing pure substances and mixtures. For example, the density of a mixture of automobile system antifreeze and water, used to prevent the engine coolant from freezing in winter or boiling in summer, varies with the composition of the mixture. Its composition and, therefore, the degree of protection that it offers against freezing can be estimated by measuring its density and relating that through a table to the freezing temperature of the mixture.

Density may be expressed in any units of mass or volume. The densities of liquids and solids are normally given in units of grams per cubic centimeter (g/cm^3, the same as grams per milliliter, g/mL). These values are convenient because they are of the order of 1 g/cm^3 for common liquids and solids.

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Table 2.2 Relationships Involving Moles of Substance

Substance	Formula unit	Formula mass	Mass of 1 mole	Numbers and kinds of individual entities in 1 mole
Helium	He atom	4.003[a]	4.003 g	6.02×10^{23} (Avogadro's number) of He atoms
Fluorine gas	F_2 molecule	38.00[b]	38.00 g	6.02×10^{23} F_2 molecules $2 \times 6.02 \times 10^{23}$ F atoms
Methane	CH_4 molecules	16.04[b]	16.04 g	6.02×10^{23} CH_4 molecules 6.02×10^{23} C atoms $4 \times 6.02 \times 10^{23}$ H atoms
Sodium oxide	Na_2O	62.00[c]	62.00 g	6.02×10^{23} Na_2O formula units $2 \times 6.02 \times 10^{23}$ Na^+ ions 6.02×10^{23} O^{2-} atoms

[a] Specifically, atomic mass
[b] Specifically, molecular mass
[c] Reference should be made to formula mass for this compound because it consists of Na^+ and S^{2-} ions in a ratio of 2/1.

The volume of a given mass of substance varies with temperature, so the density is a function of temperature. This variation is relatively small for solids, greater for liquids, and very high for gases. Densities of gases vary a great deal with pressure, as well. The temperature-dependent variation of density is an important property of water and results in stratification of bodies of water, which greatly affects the environmental chemistry that occurs in lakes and reservoirs. The density of liquid water has a maximum value of 1.0000 g/mL at 4˚C, is 0.9998 g/mL at 0˚C, and is 0.9970 g/mL at 25˚C. The combined temperature/pressure relationship for the density of air causes air to become stratified into layers, particularly the troposphere near the surface and the stratosphere from about 13 to 50 kilometers altitude.

Whereas liquids and solids have densities of the order of 1 to several g/cm^3, gases at atmospheric temperature and pressure have densities of only about one one thousandth as much (see Table 2.3 and Figure 2.4).

Table 2.3 Densities of Some Solids, Liquids, and Gases

Solids	d, g/cm^3	Liquids	d, g/cm^3	Gases	d, g/L
Sugar	1.59	Benzene	0.879	Helium	0.178
Sodium chloride	2.16	Water (4˚C)	1.0000	Methane	0.714
Iron	7.86	Carbon tetrachloride	1.595	Air	1.293
Lead	11.34	Sulfuric acid	1.84	Chlorine	3.17

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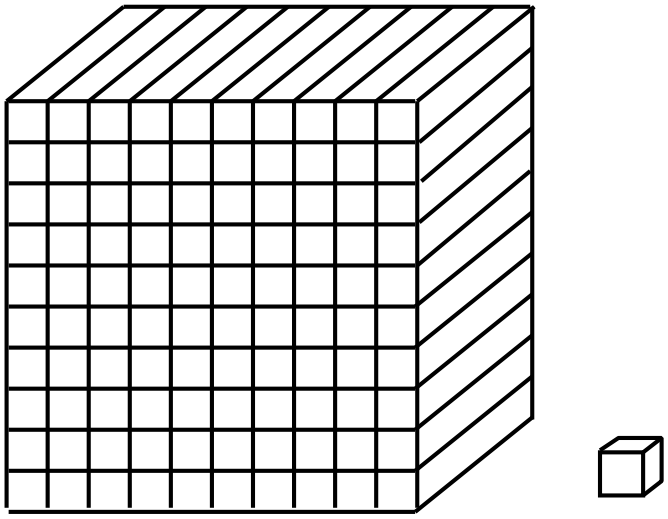


Figure 2.4 A quantity of air that occupies a volume of 1000 cm^3 of air at room temperature and atmospheric pressure (left) has about the same mass as 1 cm^3 of liquid water (right).

Specific Gravity

Often densities are expressed by means of **specific gravity** defined as the ratio of the density of a substance to that of a standard substance. For solids and liquids, the standard substance is usually water; for gases it is usually air. For example, the density of ethanol (ethyl alcohol) at 20˚C is 0.7895 g/mL. The specific gravity of ethanol at 20˚C referred to water at 4˚C is given by

$$\text{Specific gravity} = \frac{\text{density of ethanol}}{\text{density of water}} = \frac{0.7895\ \text{g/mL}}{1.0000\ \text{g/mL}} = 0.7895 \qquad (2.4.2)$$

For an exact value of specific gravity, the temperatures of the substances should be specified. In this case the notation of "specific gravity of ethanol at $^{20^\circ}/_{4^\circ}$ C" shows that the specific gravity is the ratio of the density of ethanol at 20˚C to that of water at 4˚C.

Color

Color is one of the more useful properties for identifying substances without doing any chemical or physical tests. A violet vapor, for example, is characteristic of iodine. A red/brown gas could well be bromine or nitrogen dioxide (NO_2); a practiced eye can distinguish between the two. Just a small amount of potassium permanganate, $KMnO_4$, in solution provides an intense purple color. A characteristic yellow/brown color in water may be indicative of organically bound iron.

The human eye responds to colors of electromagnetic radiation ranging in wavelength from about 400 nanometers (nm) to somewhat over 700 nm. Within this wavelength range humans see **light**; immediately below 400 nm is **ultraviolet**

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radiation, and somewhat above 700 nm is **infrared radiation** (see Figure 2.5). Light with a mixture of wavelengths throughout the visible region, such as sunlight, appears white to the eye. Light over narrower wavelength regions has the following colors: 400–450 nm, blue; 490–550 nm, green; 550–580 nm, yellow; 580–650 nm, orange, 650 nm–upper limit of visible region, red. Solutions are colored because of the light they absorb. Red, orange, and yellow solutions absorb violet and blue light; purple solutions absorb green and yellow light; and blue and green solutions absorb orange and red light. Solutions that do not absorb light are colorless (clear); solids that do not absorb light are white.

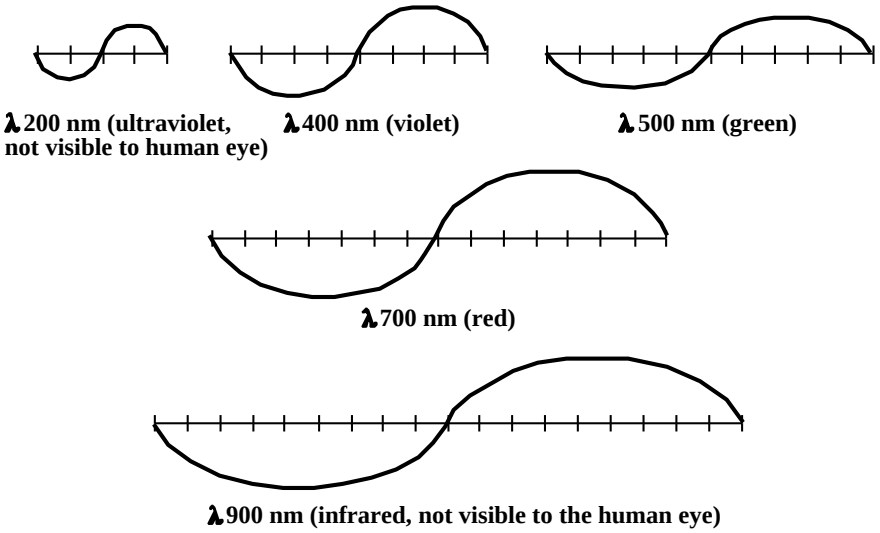


Figure 2.5 Electromagnetic radiation of different wavelengths. Each division represents 50 nm.

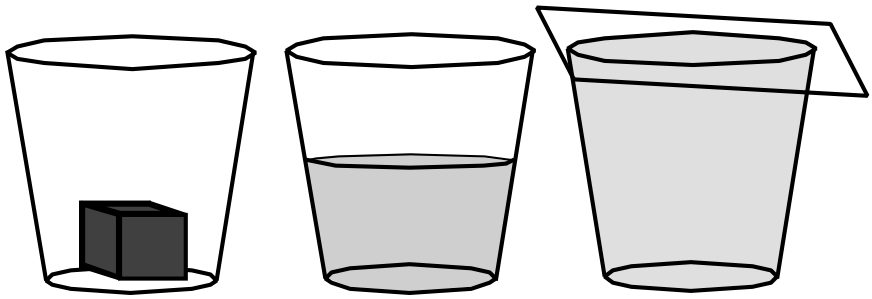
2.5 STATES OF MATTER

Figure 2.6 illustrates the three **states** in which matter can exist. **Solids** have a definite shape and volume. **Liquids** have an indefinite shape and take on the shape of the container in which they are contained. Solids and liquids are not significantly compressible, which means that a specific quantity of a substance has a definite volume and cannot be squeezed into a significantly smaller volume. **Gases** take on both the shape and volume of their containers. A quantity of gas can be compressed to a very small volume and will expand to occupy the volume of any container into which it is introduced.

Each of these separate phases is discussed in separate sections in this chapter. Everyone is familiar with the three states of matter for water. These are the following:

- Gas: Water vapor in a humid atmosphere, steam
- Liquid: Water in a lake, groundwater
- Solid: Ice in polar ice caps, snow in snowpack

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A solid has a definite shape and volume regardless of the container into which it is placed.

A quantity of liquid has a definite volume, but takes on the shape of its container.

A quantity of gas has the shape and volume of the container it occupies.

Figure 2.6 Representations of the three states of matter.

Changes in matter from one phase to another are very important in the environment. For example, water vapor changing from the gas phase to liquid results in cloud formation or precipitation. Water is desalinated by producing water vapor from sea water, leaving the solid salt behind, and recondensing the pure water vapor as a salt-free liquid. Some organic pollutants are extracted from water for chemical analysis by transferring them from the water to another organic phase that is immiscible with water. The condensation of organic pollutants from gaseous materials to solid products in the atmosphere is responsible for the visibility-reducing particulate matter in photochemical smog. Additional examples of phase changes are discussed in Section 2.10 and some of the energy relationships involved are covered in Section 2.9.

2.6 GASES

We live at the bottom of a "sea" of gas—the earth's atmosphere. It is composed of a mixture of gases, the most abundant of which are nitrogen, oxygen, argon, carbon dioxide, and water vapor. Although these gases have neither color nor odor, so that we are not aware of their presence, they are crucial to the well-being of life on Earth. Deprived of oxygen, an animal loses consciousness and dies within a short time. Nitrogen extracted from the air is converted to chemically bound forms that are crucial to plant growth. Plants require carbon dioxide and water vapor condenses to produce rain.

Gases and the atmosphere are addressed in more detail in Chapter 14. At this point, however, it is important to have a basic understanding of the nature and behavior of gases. Physically, gases are the "loosest" form of matter. A quantity of gas has neither a definite shape nor a definite volume so that it takes on the shape and volume of the container in which it is held. The reason for this behavior is that gas molecules move independently and at random, bouncing off each other as they do so. They move very rapidly; at 0˚C the average molecule of hydrogen gas moves at 3600 miles per hour, 6 to 7 times as fast as a passenger jet airplane. Gas molecules colliding with container walls exert **pressure**. An underinflated automobile tire has a low pressure because there are relatively few gas molecules in the tire to collide with

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the walls of the tire, which feel relatively soft when pushed. As more air is added the pressure is increased, the tire feels harder, and the pressure within the tire may become so high that it can no longer be contained by the tire structure so that the tire wall bursts.

A quantity of a gas is mostly empty space. That this is so is rather dramatically illustrated by comparison of the high volume of gas compared with the same amount of material in a liquid or solid. For example, at 100˚C a mole (18 g) of liquid water occupies a little more than 18 mL of volume, equivalent to just a few teaspoonfuls. When enough heat energy is added to the water to convert it all to gaseous steam at 100˚C, the volume becomes 30,600 mL, which is 1,700 times the original volume. This huge increase in volume occurs because of the large distances separating gas molecules compared with their own diameters. It is this great distance that allows gas to be compressed (pushed together). Therefore, air with a volume of more than twice that of a tire can be forced into the tire when it becomes pressurized because the air molecules can be forced closer together under the pressure in the tire when it is inflated.

The rapid, constant motion of gas molecules explains the phenomenon of gas **diffusion** in which gases move large distances from their sources. Diffusion is responsible for much of the hazard of volatile, flammable liquids, such as gasoline. Molecules of gasoline evaporated from an open container of this liquid can spread from their source. If the gaseous gasoline reaches an ignition source, such as an open flame, it may ignite and cause a fire or explosion.

The Gas Laws

To describe the physical and chemical behavior of gases, it is essential to have a rudimentary understanding of the relationships among the following: Quantity of gas in numbers of moles (n, see Section 3.2), volume (V), temperature (T), and pressure (P). These relationships are expressed by the **gas laws**. The gas laws as discussed here apply to **ideal gases**, for which it is assumed that the molecules of gas have negligible volume, that there are no forces of attraction between them, and that they collide with each other in a perfectly elastic manner. Real gases such as H_2, O_2, He, and Ar behave in a nearly ideal fashion at moderate pressures and all but very low temperatures. The gas laws were derived from observations of the effects on gas volume of changing pressure, temperature, and quantity of gas, as stated by Boyle's law, Charles' law, and Avogadro's law, respectively. These three laws are defined below:

Boyle's Law

As illustrated in Figure 2.7, doubling the pressure on a quantity of a gas halves its volume. This illustrates **Boyle's law**, according to which *at constant temperature, the volume of a fixed quantity of gas is inversely proportional to the pressure of the gas.* Boyle's law may be stated mathematically as

$$V = (\text{a constant}) \times \frac{1}{P} \qquad (2.6.1)$$

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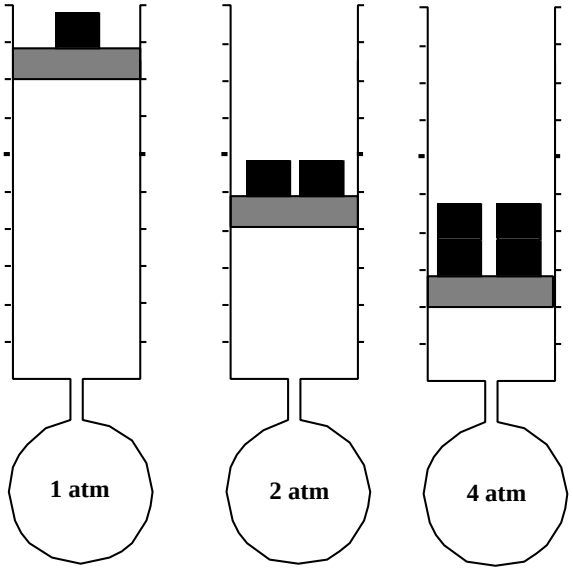


Figure 2.7 In accordance with Boyle's law, doubling the pressure of a specific quantity of gas at a constant temperature makes its volume half as great.

This inverse relationship between the volume of a gas and its pressure is a consequence of the compressibility of matter in the gas phase (recall that solids and liquids are not significantly compressible).

Charles' Law

Charles' law gives the relationship between gas volume and temperature and states that *the volume of a fixed quantity of gas is directly proportional to the absolute temperature (˚C + 273) at constant pressure*. This law may be stated mathematically as

$$V = (\text{a constant}) \times T \tag{2.6.2}$$

where T is the temperature in K (see Section 1.12). According to this relationship doubling the absolute temperature of a fixed quantity of gas at constant pressure doubles the volume.

Avogadro's Law

The third of three fundamentally important gas laws is **Avogadro's law** relating the volume of gas to its quantity in moles. This law states that *at constant temperature and pressure the volume of a gas is directly proportional to the number of molecules of gas, commonly expressed as moles*. Mathematically, this relationship is

$$V = (\text{a constant}) \times n \tag{2.6.3}$$

where n is the number of moles of gas.

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The General Gas Law

The three gas laws just defined may be combined into a **general gas law** stating that *the volume of a quantity of ideal gas is proportional to the number of moles of gas and its absolute temperature and inversely proportional to its pressure*. Mathematically, this law is

$$V = (\text{a constant}) \times \frac{nT}{P} \tag{2.6.4}$$

Designating the proportionality constant as the **ideal gas constant**, **R**, yields the **ideal gas equation**:

$$V = \frac{RnT}{P} \text{ or } PV = nRT \tag{2.6.5}$$

The units of R depend upon the way in which the ideal gas equation is used. For calculations involving volume in liters and pressures in atmospheres, the value of R is 0.0821 L-atm/deg-mol.

The ideal gas equation shows that at a chosen temperature and pressure a mole of any gas should occupy the same volume. A temperature of 0˚C (273.15 K) and 1 atm pressure have been chosen as **standard temperature and pressure** (**STP**). *At STP the volume of 1 mole of ideal gas is 22.4 L*. This volume is called the **molar volume of a gas**. It should be remembered that at a temperature of *273 K* and a pressure of *1 atm* the volume of *1 mole* of ideal gas is *22.4 L*. Knowing these values it is always possible to calculate the value of R as follows:

$$R = \frac{PV}{nT} = \frac{1 \text{ atm} \times 22.4 \text{ L}}{1 \text{ mole} \times 273 \text{ K}} = 0.0821 \frac{\text{L} \times \text{atm}}{\text{deg} \times \text{mol}} \tag{2.6.6}$$

Gas Law Calculations

A common calculation is that of the volume of a gas, starting with a particular volume and changing temperature and/or pressure. This kind of calculation follows logically from the ideal gas equation, but can also be reasoned out knowing that an *increase* in temperature causes an *increase* in volume, whereas an *increase* in pressure causes a *decrease* in volume. Therefore, a second volume, V_2, is calculated from an initial volume, V_1, by the relationship

$$V_2 = V_1 \times \frac{\square}{\square} \times \frac{\square}{\square} \tag{2.6.7}$$

Ratio of temperatures **Ratio of pressures**

This relationship requires only that one remember the following:

- If the temperature *increases* (if T_2 is greater than T_1), the volume *increases*. Therefore, T_2 is always placed over T_1 in the ratio of temperatures.

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- If the pressure *increases* (if P_2 is greater than P_1), the volume *decreases.* Therefore, P_1 is always placed over P_2 in the ratio of pressures.
- If there is no change in temperature or pressure, the corresponding ratio remains 1.

These relationships can be illustrated by several examples.

Charles' Law Calculation

When the temperature of a quantity of gas changes while the pressure stays the same, the resulting calculation is a *Charles' law calculation.* As an example of such a calculation, calculate the volume of a gas with an initial volume of 10.0 L when the temperature changes from -11.0˚C to 95.0˚C at constant pressure. The first step in solving any gas law problem involving a temperature change is to convert Celsius temperatures to kelvin:

$$T_1 = 273 + (-11) = 262 \text{ K} \qquad T_2 = 273 + 95 = 368 \text{ K}$$

Substitution into Equation 2.6.7 gives

$$V_2 = V_1 \times \frac{368 \text{ K}}{262 \text{ K}} \times 1(\text{factor for pressure} = 1 \text{ because } P_2 = P_1) \tag{2.6.8}$$

$$V_2 = 10.0 \text{ L} \times \frac{368 \text{ K}}{262 \text{ K}} = 14.0 \text{ L}$$

Note that in this calculation it is seen that the temperature increases, this increases the volume, so the higher temperature is placed over the lower. Furthermore, since $P_2 = P_1$, the factor for the pressure ratio simply drops out.

Calculate next the volume of a gas with an initial volume of 10.0 L after the temperature decreases from 111.0˚C to 2.0˚C at constant pressure:

$$T_1 = 273 + (111) = 384 \text{ K} \qquad T_2 = 273 + 2 = 275 \text{ K}$$

Substitution into Equation 2.6.6 gives

$$V_2 = V_1 \times \frac{275 \text{ K}}{384 \text{ K}} = 10.0 \text{ L} \times \frac{275 \text{ K}}{384 \text{ K}} \tag{2.6.9}$$

$$= 7.16 \text{ L}$$

In this calculation the temperature decreases, this decreases the volume, so the lower temperature is placed over the higher (mathematically it is still T_2 over T_1 regardless of which way the temperature changes).

Boyle's Law Calculation

When the pressure of a quantity of gas changes while the temperature stays the same, the resulting calculation is a *Boyle's law calculation.* As an example,

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calculate the new volume that results when the pressure of a quantity of gas initially occupying 12.0 L is changed from 0.856 atm to 1.27 atm at constant temperature. In this case, the pressure has increased, this decreases the volume of the gas so that V_2 is given by the following:

$$V_2 = V_1 \times \frac{0.856 \text{ atm}}{1.27 \text{ atm}} \times 1 \text{ (because } T_2 = T_1) = 12.0 \text{ L} \times \frac{0.856 \text{ atm}}{1.27 \text{ atm}} \quad (2.6.10)$$

$$= 8.09 \text{ L}$$

Calculate next the volume of a gas with an initial volume of 15.0 L when the pressure decreases from 1.71 atm to 1.07 atm at constant temperature. In this case the pressure decreases, this increases the volume, so the appropriate factor to multiply by is 1.71/1.07:

$$V_2 = V_1 \times \frac{1.71 \text{ atm}}{1.07 \text{ atm}} = 15.0 \text{ L} \times \frac{1.71 \text{ atm}}{1.07 \text{ atm}} = 24.0 \text{ L} \quad (2.6.11)$$

Calculations Using the Ideal Gas Law:

The ideal gas law equation

$$PV = nRT \quad (2.6.5)$$

may be used to calculate any of the variables in it if the others are known. As an example, calculate the volume of 0.333 moles of gas at 300 K under a pressure of 0.950 atm:

$$V = \frac{nRT}{P} = \frac{0.333 \text{ mol} \times 0.0821 \text{ L atm/K mol} \times 300 \text{ K}}{0.950 \text{ atm}} = 8.63 \text{ L} \quad (2.6.12)$$

As another example, calculate the temperature of 2.50 mol of gas that occupies a volume of 52.6 L under a pressure of 1.15 atm:

$$T = \frac{PV}{nR} = \frac{1.15 \text{ atm} \times 52.6 \text{ L}}{2.50 \text{ mol} \times 0.0821 \text{ L atm/K mol}} = 295 \text{ K} \quad (2.6.13)$$

Other examples of gas law calculations are given in the problem section at the end of this chapter.

Where subscripts 1 and 2 denote parameters before and after any change, respectively, the following relationship can be derived from the fact that R is a constant in the ideal gas law equation:

$$\frac{P_2V_2}{n_2T_2} = \frac{P_1V_1}{n_1T_1} \quad (2.6.14)$$

derived from the fact that R is a constant, where the subscripts 1 and 2 denote values of the parameters designated before and after these are changed. By holding the appropriate parameters constant, this equation can be used to derive the mathematical relationships used in calculations involving Boyle's law, Charles' law, or Avogadro's law, as well as any combination of these laws.

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Exercise: Derive an equation that will give the volume of a gas after all three of the parameters P, T, and n have been changed.

Answer: Rearrangement of Equation 2.6.13 gives the relationship needed:

$$V_2 = V_1 \frac{P_1 n_2 T_2}{P_2 n_1 T_1} \qquad (2.6.15)$$

2.7 LIQUIDS AND SOLUTIONS

Whereas the molecules in gases are relatively far apart and have minimal attractive forces among them (none in the case of ideal gases, discussed in the preceding section), molecules of liquids are close enough together that they can be regarded as "touching" and are strongly attracted to each other. Like those of gases, however, the molecules of liquids move freely relative to each other. These characteristics give rise to several significant properties of liquids. Whereas gases are mostly empty space, most of the volume of a liquid is occupied by molecules; therefore, the densities of liquids are much higher than those of gases. Because there is little unoccupied space between molecules of liquid, liquids are only slightly *compressible*; doubling the pressure on a liquid causes a barely perceptible change in volume, whereas it halves the volume of an ideal gas. Liquids do not expand to fill their containers as do gases. Essentially, therefore, a given quantity of liquid occupies a fixed volume. Because of the free movement of molecules relative to each other in a liquid, it takes on the shape of that portion of the container that it occupies.

Evaporation and Condensation of Liquids

Consider the surface of a body of water as illustrated in Figure 2.8. The molecules of liquid water are in constant motion relative to each other. They have a distribution of energies such that there are more higher energy molecules at higher temperatures. Some molecules are energetic enough that they escape the attractive forces of the other molecules in the mass of liquid and enter the gas phase. This phenomenon is called **evaporation**.

Molecules of liquid in the gas phase, such as water vapor molecules above a body of water, may come together or strike the surface of the liquid and reenter the liquid phase. This process is called **condensation**. It is what happens, for example, when water vapor molecules in the atmosphere strike the surface of very small water droplets in clouds and enter the liquid water phase, causing the droplets to grow to sufficient size to fall as precipitation.

Vapor Pressure

In a confined area above a liquid, equilibrium is established between the evaporation and condensation of molecules from the liquid. For a given temperature, this results in a steady-state level of the vapor, which can be described as a pressure. Such a pressure is called the **vapor pressure** of the liquid (see Figure 2.8).

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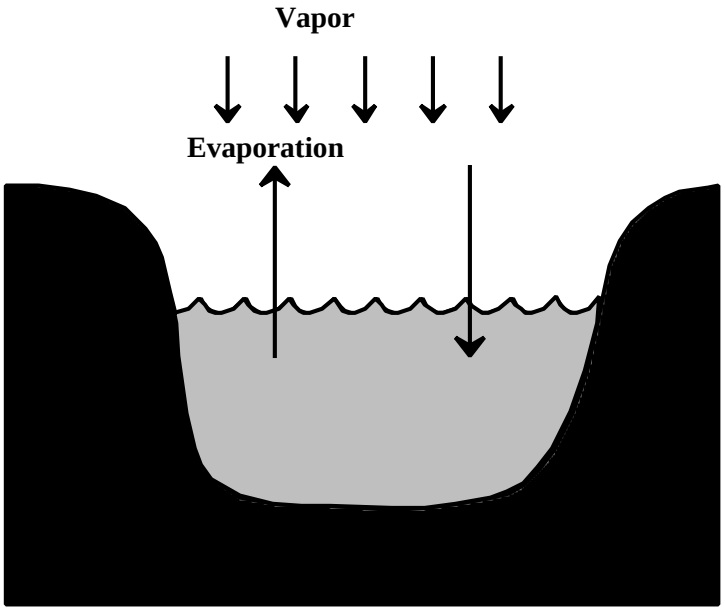


Figure 2.8 Evaporation and condensation of liquid.

Vapor pressure is very important in determining the fates and effects of substances, including hazardous substances, in the environment. Loss of a liquid by evaporation to the atmosphere increases with increasing vapor pressure and is an important mechanism by which volatile pollutants enter the atmosphere. High vapor pressure of a flammable liquid can result in the formation of explosive mixtures of vapor above a liquid, such as in a storage tank.

Solutions

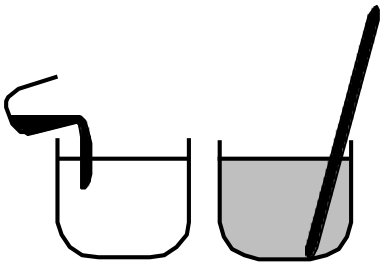
Solutions were mentioned in Section 2.2 as homogeneous mixtures. Here solutions are regarded as liquids in which quantities of gases, solids, or other liquids are dispersed as individual ions or molecules. Rainwater, for example, is a solution containing molecules of N_2, O_2 and CO_2 from air dispersed among the water molecules. Rainwater from polluted air may contain harmful substances such as sulfuric acid (H_2SO_4) in small quantities among the water molecules. The predominant liquid constituent of a solution is called the **solvent**. A substance dispersed in it is said to be **dissolved** in the solvent and is called the **solute**.

Solubility

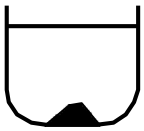
Mixing and stirring some solids, such as sugar, with water results in a rapid and obvious change in which all or part of the substance seems to disappear as it dissolves. When this happens, the substance is said to *dissolve*, and one that does so to a significant extent is said to be **soluble** in the solvent. Substances that do not dissolve to a perceptible degree are called **insoluble**. *Solubility* is a significant

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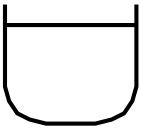
physical property. It is a relative term. For example, Teflon is insoluble in water, limestone is slightly soluble, and ethanol (ethyl alcohol) is infinitely so in that it can be mixed with water in any proportion ranging from pure water to pure ethanol with only a single liquid phase consisting of an ethanol/water solution being observed.



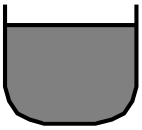
Whether a solid dissolves significantly in water may be determined in the laboratory by stirring the solid with water in a beaker.



An insoluble substance will show no evidence of dissolving and will remain as a residue in the beaker.



An appreciably soluble substance will seem to disappear, leaving only liquid



If the dissolved substance absorbs light, the solution formed will be colored; the color may be useful to identify the substance.

Figure 2.9 Illustration of whether a substance dissolves in a liquid.

Solution Concentration

Solutions are addressed specifically and in more detail in Chapter 7. At this point, however, it is useful to have some understanding of the quantitative expression of the amount of solute dissolved in a specified amount of solution. In a relative sense, a solution that has comparatively little solute dissolved per unit volume of solution is called a **dilute solution**, whereas one with an amount of solute of the same order of magnitude as that of the solvent is a **concentrated solution**. Water saturated with air at 25˚C contains only about 8 milligrams of oxygen dissolved in 1 liter of water; this composes a *dilute solution* of oxygen. A typical engine coolant solution contains about as much ethylene glycol (antifreeze) as it does water, so it is a *concentrated solution*. A solution that is at equilibrium with excess solute so that it contains the maximum amount of solute that it can dissolve is called a **saturated solution**. One that can still dissolve more solute is called an **unsaturated solution**.

For the chemist, the most useful way to express the concentration of a solution is in terms of the number of moles of solute dissolved per liter of solution. The **molar concentration**, **M**, of a solution is *the number of moles of solute dissolved per liter of solution.* Mathematically,

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$$M = \frac{\text{moles of solute}}{\text{number of liters of solution}} \quad (2.7.1)$$

Example: Exactly 34.0 g of ammonia, NH_3, were dissolved in water and the solution was made up to a volume of exactly 0.500 L. What was the molar concentration, M, of ammonia in the resulting solution?

Answer: The molar mass of NH_3 is 17.0 g/mole. Therefore

$$\text{Number of moles of } NH_3 = \frac{34.0 \text{ g}}{17.0 \text{ g/mole}} = 2.00 \text{ mol} \quad (2.7.2)$$

The molar concentration of the solution is calculated from Equation 2.7.1:

$$M = \frac{2.00 \text{ mol}}{0.500 \text{ L}} = 4.00 \text{ mol/L} \quad (2.7.3)$$

Equations 2.7.1 and 2.7.2 are useful in doing calculations that relate mass of solute to solution volume and solution concentration in chemistry (see stoichiometry in Chapter 6).

2.8 SOLIDS

Matter in the form of *solids* is said to be in the **solid state**. The solid state is the most organized form of matter in that the atoms, molecules, and ions in it are in essentially fixed relative positions and are highly attracted to each other. Therefore, solids have a definite shape, maintain a constant volume, are virtually non-compressible under pressure, and expand and contract only slightly with changes in temperature. Like liquids, solids have generally very high densities relative to gases. (Some solids such as those made from styrofoam appear to have very low densities, but that is because such materials are composed mostly of bubbles of air in a solid matrix.) Because of the strong attraction of the atoms, molecules, and ions of solids for each other, solids do not enter the vapor phase very readily at all; the phenomenon by which this happens to a limited extent is called **sublimation**.

Some solids (quartz, sodium chloride) have very well defined geometric shapes and form characteristic crystals. These are called **crystalline solids** and occur because the molecules or ions of which they are composed assume well defined, specific positions relative to each other. Other solids have indefinite shapes because their constituents are arranged at random; glass is such a solid. These are **amorphous solids**.

2.9 THERMAL PROPERTIES

The behavior of a substance when heated or cooled defines several important physical properties of it, including the temperature at which it melts or vaporizes. Also included are the amounts of heat required by a given mass of the substance to raise its temperature by a unit of temperature, to melt it, or to vaporize it.

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Melting Point

The **melting point** of a pure substance is the temperature at which the substance changes from a solid to a liquid. At the melting temperature, pure solid and pure liquid composed of the substance may be present together in a state of equilibrium. An impure substance does not have a single melting temperature. Instead, as heat is applied to the substance, it begins to melt at a temperature below the melting temperature of the pure substance; melting proceeds as the temperature increases until no solid remains. Therefore, melting temperature measurements serve two purposes in characterizing a substance. The melting point of a pure substance is indicative of the identity of the substance. The melting behavior—whether melting occurs at a single temperature or over a temperature range—is a measure of substance purity.

Boiling Point

Boiling occurs when a liquid is heated to a temperature such that bubbles of vapor of the substance are evolved. The boiling temperature depends upon pressure, and reduced pressures can be used to cause liquids to boil at lower temperatures. When the surface of a pure liquid substance is in contact with the pure vapor of the substance at 1 atm pressure, boiling occurs at a temperature called the **normal boiling point** (see Figure 2.10). Whereas a pure liquid remains at a constant temperature during boiling until it has all turned to vapor, the temperature of an impure liquid increases during boiling. As with melting point, the boiling point is useful for identifying liquids. The extent to which the boiling temperature is constant as the liquid is converted to vapor is a measure of the purity of the liquid.

Specific Heat

As the temperature of a substance is raised, energy must be put into it to enable the molecules of the substance to move more rapidly relative to each other and to overcome the attractive forces between them. The amount of heat energy required to raise the temperature of a unit mass of a solid or liquid substance by a degree of temperature varies with the substance. Of the common liquids, the most heat is required to raise the temperature of water. This is because of the molecular structure of water, the molecules of which are strongly attracted to each other by electrical charges between the molecules (each of which has a relatively positive and a relatively more negative end). Furthermore, water molecules tend to be held in molecular networks by special kinds of chemical bonds called hydrogen bonds, in which hydrogen atoms form bridges between O atoms in different water molecules. The very high amount of energy required to increase the temperature of water has some important environmental implications because it stabilizes the temperatures of bodies of water and of geographic areas close to bodies of water. In contrast to water, hydrocarbon liquids such as those in gasoline require relatively little heat for warming because the molecules interact much less with each other than do those of water.

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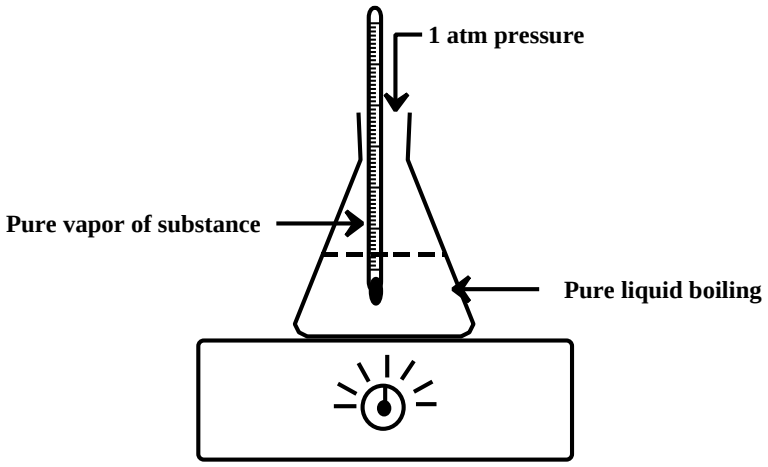


Figure 2.10 Illustration of normal boiling liquid.

The heat required to raise the temperature of a substance is called the **specific heat**, defined as the amount of heat energy required to raise the temperature of a gram of substance by 1 degree Celsius. It can be expressed by the equation

$$\text{Specific heat} = \frac{\text{heat energy absorbed, J}}{(\text{mass, g})(\text{increase in temperature, }^{\circ}\text{C})} \qquad (2.9.1)$$

where the heat energy is in units of joule, J. The most important value of specific heat is that of water, 4.18 J/g˚C. From Equation 2.9.1, the amount of heat, q, required to raise the mass, m, of a particular substance over a temperature range of ΔT is

$$q = (\text{specific heat}) \times m \times \Delta T \qquad (2.9.2)$$

This equation can be used to calculate quantities of heat used in increasing water temperature or released when water temperature decreases. As an example, consider the amount of heat required to raise the temperature of 11.6 g of liquid water from 14.3˚C to 21.8˚C:

$$q = 4.18 \frac{\text{J}}{\text{g}^{\circ}\text{C}} \times 11.6\ \text{g} \times (21.8^{\circ}\text{C} - 14.3^{\circ}\text{C}) = 364\ \text{J} \qquad (2.9.2)$$

Heat of Vaporization

Large amounts of heat energy may be required to convert liquid to vapor compared with the specific heat of the liquid. This is because changing a liquid to a gas requires breaking the molecules of liquid away from each other, not just increasing the rates at which they move relative to one another. The vaporization of a pure liquid occurs at a constant temperature (normal boiling temperature, see above). For

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example, the temperature of a quantity of pure water is increased by heating to 100˚C where it remains until all the water has evaporated. The **heat of vaporization** is the quantity of heat taken up in converting a unit mass of liquid entirely to vapor at a constant temperature. The heat of vaporization of water is 2,260 J/g (2.26 kJ/g) for water boiling at 100˚C at 1 atm pressure. This amount of heat energy is about 540 times that required to raise the temperature of 1 gram of liquid water by 1˚C. The fact that water's heat of vaporization is the largest of any common liquid has significant environmental effects. It means that enormous amounts of heat are required to produce water vapor from liquid water in bodies of water. This means that the temperature of a body of water is relatively stable when it is exposed to high temperatures because so much heat is dissipated when a fraction of the water evaporates. When water vapor condenses, similar enormous amounts of heat energy, called **heat of condensation**, are released. This occurs when water vapor forms precipitation in storm clouds and is the driving force behind the tremendous releases of heat that occur in thunderstorms and hurricanes.

The heat of vaporization of water can be used to calculate the heat required to evaporate a quantity of water. For example, the heat, q, required to evaporate 2.50 g of liquid water is

$$q = (\text{heat of vaporization})(\text{mass of water}) = 2.26\ \text{kJ/g} \times 2.50\ \text{g} = 5.65\ \text{kJ} \quad (2.9.3)$$

and that released when 5.00 g of water vapor condenses is

$$q = -(\text{heat of vaporization})(\text{mass of water}) = -2.26\ \text{kJ/g} \times 5.00\ \text{g} = -11.3\ \text{kJ} \quad (2.9.4)$$

the latter value is negative to express the fact that heat is *released*.

Heat of Fusion

Heat of fusion is the quantity of heat taken up in converting a unit mass of solid entirely to liquid at a constant temperature. The heat of fusion of water is 330 J/g for ice melting at 0˚C. This amount of heat energy is 80 times that required to raise the temperature of 1 gram of liquid water by 1˚C. When liquid water freezes, an exactly equal amount of energy per unit mass is released, but is denoted as a negative value.

The heat of fusion of water can be used to calculate the heat required to melt a quantity of ice. For example, the heat, q, required to melt 2.50 g of ice is

$$q = (\text{heat of fusion})(\text{mass of water}) = 330\ \text{J/g} \times 2.50\ \text{g} = 825\ \text{J} \quad (2.9.5)$$

and that released when 5.00 g of liquid water freezes is

$$q = -(\text{heat of fusion})(\text{mass of water}) = -330\ \text{J/g} \times 5.00\ \text{g} = -1{,}650\ \text{J} \quad (2.9.6)$$

2.10 SEPARATION AND CHARACTERIZATION OF MATTER

A very important aspect of the understanding of matter is the separation of mixtures of matter into their consituent pure substances. Consider, the treatment of

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an uncharacterized waste sludge found improperly disposed of in barrels. Typically, the sludge will appear as a black goo with an obnoxious odor from several constituents. In order to do a proper analysis of this material, it often needs to be separated into its constituent components, such as by extracting water-soluble substances into water, extracting organic materials into an organic solvent, and distilling off volatile constituents. The materials thus isolated can be analyzed to determine what is present. With this knowledge and with information about the separation itself a strategy can be devised to treat the waste in an effective, economical manner.

Many kinds of processes are used for separations, and it is beyond the scope of this chapter to go into detail about them here. However, several of the more important separation operations are discussed briefly below.

Distillation

Distillation consists of evaporating a liquid by heating and cooling the vapor so that it condenses back to the liquid in a different container, as shown for water in Figure 2.11. Less-volatile constituents such as solids are left behind in the distillation flask; more-volatile impurities such as volatile organic compound pollutants in water will distill off first and can be placed in different containers before the major liquid constituent is collected.

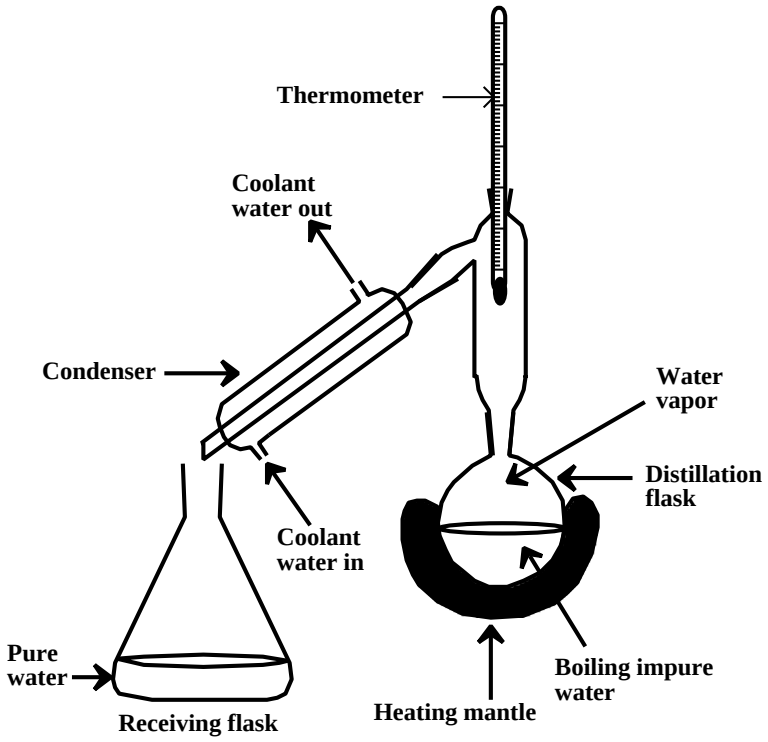


Figure 2.11 Separation by distillation.

The apparatus shown in Figure 2.11 could be used, for example, to prepare fresh water from seawater, which can be considered a solution of sodium chloride in

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water. The seawater to be purified is placed in a round-bottom distillation flask heated with an electrically powered heating mantle. The seawater is boiled and pure water vapor in the gaseous state flows into the condenser where it is cooled and condensed back to a purified salt-free product in the receiving flask. When most of the seawater has been evaporated, the distillation flask and its contents are cooled and part of the sodium chloride separates out as crystals that can be removed. Sophisticated versions of this distillation process are used in some arid regions of the world to produce potable (drinking) water from seawater.

Distillation is widely used in the petroleum and chemical industries. A sophisticated distillation apparatus is used to separate the numerous organic components of crude oil, including petroleum ether, gasoline, kerosene, and jet fuel fractions. This requires **fractional distillation** in which part of the vapor recondenses in a **fractionating column** that would be mounted vertically on top of the distillation flask in the apparatus shown in Figure 2.11. The most volatile components enter into the condenser and are condensed back to liquid products; less volatile liquid constituents return to the distillation flask. The net effect is that of numerous distillations, which gives a very efficient separation.

In some cases the residues left from distillation, **distillation bottoms** ("still bottoms") are waste materials. Several important categories of hazardous wastes consist of distillation bottoms, which pose disposal problems.

Separation in Waste Treatment

In addition to distillation, several other kinds of separation procedures are used for waste treatment. These are addressed in more detail in Chapter 22 and are mentioned here as examples of separation processes.

Phase Transitions

Distillation is an example of a separation in which one of the constituents being separated undergoes a **phase transition** from one phase to another, then often back again to the same phase. In distillation, for example, a liquid is converted to the vapor state, then recondensed as a liquid. Several other kinds of separations by phase transition as applied to waste treatment are the following:

Evaporation is usually employed to remove water from an aqueous waste to concentrate it. A special case of this technique is **thin-film evaporation**, in which volatile constituents are removed by heating a thin layer of liquid or sludge waste spread on a heated surface.

Drying—removal of solvent or water from a solid or semisolid (sludge) or the removal of solvent from a liquid or suspension—is a very important operation because water is often the major constituent of waste products, such as sludges. In **freeze drying**, the solvent, usually water, is sublimed from a frozen material. Hazardous-waste solids and sludges are dried to reduce the quantity of waste, to remove solvent or water that might interfere with subsequent treatment processes, and to remove hazardous volatile constituents.

Stripping is a means of separating volatile components from less-volatile ones in a liquid mixture by the partitioning of the more-volatile materials to a gas phase of

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air or steam (steam stripping). The gas phase is introduced into the aqueous solution or suspension containing the waste in a stripping tower that is equipped with trays or packed to provide maximum turbulence and contact between the liquid and gas phases. The two major products are condensed vapor and a stripped bottoms residue. Examples of two volatile components that can be removed from water by air stripping are the organic solvents benzene and dichloromethane.

Physical precipitation is used here as a term to describe processes in which a dissolved solute comes out of solution as a solid as a result of a physical change in the solution. The major changes that can cause physical precipitation are cooling the solution, evaporation of solvent, or alteration of solvent composition. The most common type of physical precipitation by alteration of solvent composition occurs when a water-miscible organic solvent is added to an aqueous (water) solution of a salt, so that the solubility of a salt is lowered below its concentration in the solution.

Phase Transfer

Phase transfer consists of the transfer of a solute in a mixture from one phase to another. An important type of phase transfer process is **solvent extraction**, shown in Figure 2.12, a process in which a substance is transferred from solution in one solvent (usually water) to another (usually an organic solvent) without any chemical change taking place. When solvents are used to leach substances from solids or sludges, the process is called **leachin**g. One of the more promising approaches to solvent extraction and leaching of hazardous wastes is the use of supercritical fluids, most commonly CO_2, as extraction solvents. A supercritical fluid is one that has char-

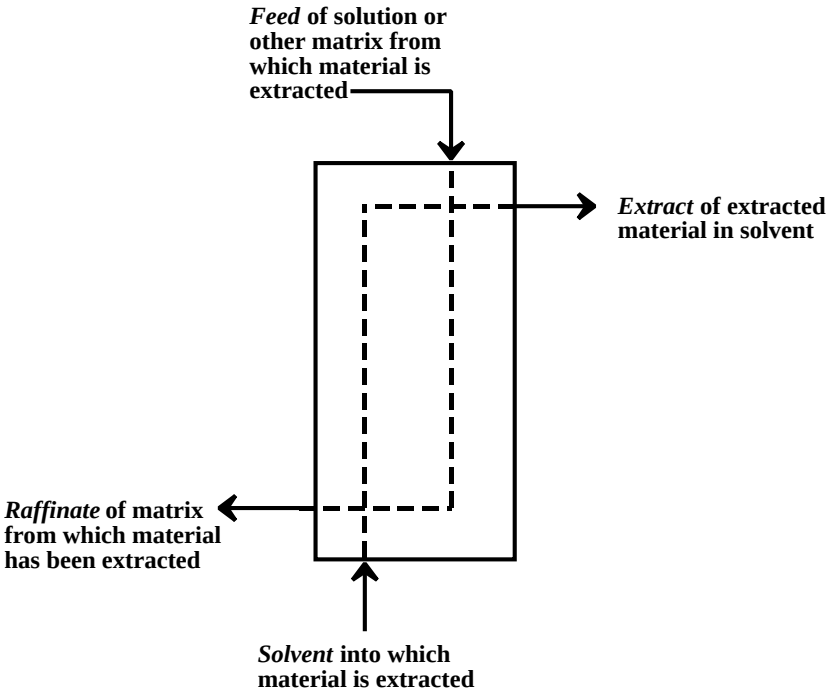


Figure 2.12 Outline of solvent extraction/leaching process with important terms in italics.

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acteristics of both liquid and gas and consists of a substance above its supercritical temperature and pressure (31.1˚C and 73.8 atm, respectively, for CO_2). After a substance has been extracted from a waste into a supercritical fluid at high pressure, the pressure can be released, resulting in separation of the substance extracted. The fluid can then be compressed again and recirculated through the extraction system. Some possibilities for treatment of hazardous wastes by extraction with supercritical CO_2 include removal of organic contaminants from wastewater, extraction of organohalide pesticides from soil, extraction of oil from emulsions used in aluminum and steel processing, and regeneration of spent activated carbon.

Transfer of a substance from a solution to a solid phase is called **sorption**. The most important sorbent used in waste treatment is **activated carbon**. Activated carbon can also be applied to pretreatment of waste streams going into other processes to improve treatment efficiency and reduce fouling. Activated carbon sorption is most effective for removing from water organic materials that are poorly water soluble and that have high molecular masses.

Molecular Separation

A third major class of physical separation is **molecular separation**, often based upon **membrane processes** in which dissolved contaminants or solvent pass through a size-selective membrane under pressure. **Reverse osmosis** is the most widely used of the membrane techniques. It operates by virtue of a membrane that is selectively permeable to water and excludes ionic solutes. Reverse osmosis uses high pressures to force permeate through the membrane, producing a concentrate containing high levels of dissolved salts.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Matter is defined as [1]_____. Chemical properties of matter are those that are observed [2]_____, whereas physical properties are those that are observed [3]_____. Matter consists of only a few [4]_____ and a large number of substances formed from them called [5]_____. Some general properties of metals are [6]_____. Some common properties of nonmetals are [7]_____. [8]_____ substances consist of virtually all compounds that contain carbon, whereas [9]_____ substances make up virtually all

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matter that does not contain carbon. Matter consisting of [10]_____ _____ is a pure substance; any other form of matter is a [11]_____ of two or more substances. A [12]_____is not uniform throughout and possesses readily distinguishable constituents, whereas [13]_____ _____ are uniform throughout. A mole is defined as the quantity of substance that [14]_____ _____. A mole of H_2O contains [15]_____ grams of this compound. Avogadro's number is the number of specified entities [16]_____ and it has a value of [17]_____. A general term that includes atoms and molecules as well as groups of ions making up the smallest possible quantity of an ionic compound is the [18]_____. The average mass of a formula unit is called the [19]_____. Density is defined as [20]_____ and expressed by the formula [21]_____. Relative densities are expressed by means of a number called [22]_____ defined as [23]_____ _____. Some solutions are colored because they [24]_____ _____. Solids, liquids, and gases are the three [25]_____ of matter. A solid has a definite [26]_____ and [27]_____ regardless of the container in which it is placed, a liquid has a definite [28]_____, but takes on the [29]_____ of its container, and a gas has the same [30]_____ as its container. Gas molecules move [31]_____, colliding with container walls to exert [32]_____. A quantity of a gas has a [33]_____ compared with the same amount of material in a liquid or solid. [34]_____ enables gas molecules to move large distances from their sources. The gas laws relate the four parameters of [35]_____ _____ of gas. Boyle's law states that [36] _____ _____. Charles' law states that [37]_____ _____. Avogadro's law states that [38] _____ _____. The general gas law states that [39] _____ _____. The ideal gas law is given mathematically as [40] _____. At a temperature of 0˚C and 1 atm pressure known as [41] _____ the volume of 1 mole of ideal gas is [42] _____. Molecules of liquids move [43] _____ relative to each other. Because there is little unoccupied space between molecules of liquid, liquids are only slightly [44]_____. The phenomenon by which molecules of liquid enter the gas phase is called [45] _____, whereas the opposite phenomenon is termed [46] _____. A steady-state level of the vapor of a liquid above the liquid surface is called the [47] _____ _____ of the liquid. Solutions are regarded as liquids in which [48] _____ _____.

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The predominant liquid constituent of a solution is called the [49] _____, a substance dispersed in it is said to be [50] _____ in the solvent and is called the [51] _____. A substance that dissolves to a significant extent is said to be [52] _____ in the solvent. Substances that do not dissolve to a perceptible degree are classified as [53] _____. A solution that has comparatively little solute dissolved per unit volume of solution is called a [54] _____ _____ solution, whereas one with an amount of solute of the same order of magnitude as that of the solvent is a [55] _____ solution. The molar concentration, M, of a solution is defined as [56]_____ and is given by formula [57] _____. The solid state is the most [58] _____ form of matter because the atoms, molecules, and ions in it are [59] _____ _____.The phenomenon by which solids enter the gaseous state directly is called [60] _____. Solids that form well-defined crystals are called [61] _____. and those that have indefinite shapes because their constituents are arranged at random are called [62] _____. The melting point of a pure substance is the temperature at which the substance changes [63] _____ _____. At this temperature, pure solid and pure liquid composed of the substance [64]_____. A(n) impure substance does not have [65] _____. The two purposes served by melting temperature measurements in characterizing a substance are [66] _____ _____ and [67]_____ _____. When a pure liquid is heated such that the surface of the liquid is in contact with the pure vapor of the substance at 1 atm pressure, boiling occurs at a temperature called the [68] _____. The extent to which the boiling temperature is constant as the liquid is converted to vapor is a measure [69] _____. The amount of heat energy required to raise the temperature of a unit mass of a solid or liquid substance by a degree of temperature is called the [70] _____of the substance and can be expressed by the equation [71] _____. The heat of vaporization is defined as [72] _____ _____. Mathematically, the heat, q, required to evaporate a specified mass of liquid water is [73] _____. Heat of fusion is defined as [74] _____ _____. Distillation consists of [75] _____ _____. Fractional distillation is a separation process in which part of the vapor [76] _____ _____. Residues left from distillation are called [77] _____. A process in which a solvent is sublimed from a frozen material is called [78] _____. Stripping is a means of separating volatile components from less-volatile ones in a liquid mixture by [79] _____

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_____. Solvent extraction is a process in which [80] _____ _____. The most important sorbent used in waste treatment is [81] _____. A water purification process called [82] _____ uses high pressures to force permeate through a membrane that is selectively permeable to water and excludes ionic solutes.

Answers to Chapter Summary

1. anything that has mass and occupies space
2. by chemical change or the potential for chemical change
3. without any chemical change
4. elements
5. compounds
6. generally solid, shiny in appearance, electrically conducting, and malleable
7. a dull appearance, not at all malleable, and frequently present as gases or liquids
8. Organic
9. inorganic substances
10. only one compound or of only one form of an element
11. mixture
12. heterogeneous mixture
13. homogeneous mixtures
14. contains the same number of specified entities as there are atoms of C in exactly 0.012 kg (12 g) of carbon-12
15. 18
16. in a mole of substance
17. 6.02×10^{23}
18. formula unit
19. formula mass
20. mass per unit volume
21. d = mass/volume
22. specific gravity
23. the ratio of the density of a substance to that of a standard substance
24. absorb light
25. states
26. shape
27. volume
28. volume
29. shape
30. shape and volume
31. independently and at random
32. pressure
33. high volume
34. Diffusion
35. moles (n), volume (V), temperature (T), and pressure (P)
36. at constant temperature, the volume of a fixed quantity of gas is inversely

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proportional to the pressure of the gas
37. the volume of a fixed quantity of gas is directly proportional to the absolute temperature at constant pressure
38. at constant temperature and pressure the volume of a gas is directly proportional to the number of molecules of gas, commonly expressed as moles
39. the volume of a quantity of ideal gas is proportional to the number of moles of gas and its absolute temperature and inversely proportional to its pressure
40. $PV = nRT$
41. standard temperature and pressure (STP)
42. 22.4 L
43. freely
44. compressible
45. evaporation
46. condensation
47. vapor pressure
48. quantities of gases, solids, or other liquids are dispersed as individual ions or molecules
49. solvent
50. dissolved
51. solute
52. soluble
53. insoluble
54. dilute
55. concentrated
56. the number of moles of solute dissolved per liter of solution
57. $M = \dfrac{\text{moles of solute}}{\text{number of liters of solution}}$
58. organized
59. in essentially fixed relative positions and are highly attracted to each other
60. sublimation
61. crystalline solids
62. amorphous solids
63. from a solid to a liquid
64. may be present together in a state of equilibrium
65. a single melting temperature
66. the melting point of a pure substance is indicative of the identity of the substance
67. the melting behavior—whether melting occurs at a single temperature or over a temperature range—is a measure of substance purity
68. normal boiling point
69. of the purity of the liquid
70. specific heat
71. $\text{Specific heat} = \dfrac{\text{heat energy absorbed, J}}{(\text{mass, g})(\text{increase in temperature, }^{\circ}\text{C})}$
72. the quantity of heat taken up in converting a unit mass of liquid entirely to vapor at a constant temperature
73. q = (heat of vaporization)(mass of water)
74. the quantity of heat taken up in converting a unit mass of solid entirely to liquid

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at a constant temperature
75. evaporating a liquid by heating and cooling the vapor so that it condenses back to the liquid in a different container
76. recondenses in a fractionating column
77. distillation bottoms
78. freeze drying
79. the partitioning of the more-volatile materials to a gas phase of air or steam
80. a substance is transferred from solution in one solvent to another without any chemical change taking place
81. activated carbon
82. Reverse osmosis

QUESTIONS AND PROBLEMS

Section 2.1. What is Matter

1. What is the definition of matter?

Section 2.2. Classification of Matter

2. Classify each of the following as chemical processes (c) or physical processes (p):

 () Ice melts
 () $CaO + H_2O \rightarrow Ca(OH)_2$
 () A small silver sphere pounded into a thin sheet
 () A copper-covered roof turns green in the atmosphere
 () Wood burns
 () Oxygen isolated by the distillation of liquid air

3. List (a) three common characteristics of metals and (b) three common characteristics of nonmetals.

4. Classify each of the following as organic substances (o) or inorganic substances (i):

 () Crude oil
 () A dime coin
 () A shirt
 () Asphalt isolated as a residue of petroleum distillation
 () A compound composed of silicon, oxygen, and aluminum
 () Concrete

5. Sandy sediment from the bottom of a river was filtered to isolate a clear liquid, which was distilled to give a liquid compound that could not be broken down further by non-chemical means. Explain how these operations illustrate heterogeneous mixtures, homogeneous mixtures, and pure substances.

6. Explain why a solution is defined as a homogeneous mixture.

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Section 2.3. Quantity of Matter: The Mole

7. Justify the statement that "exactly 12 g of carbon-12 contain 6.02 x 10^{23} atoms of the isotope of carbon that contains 6 protons and 6 neutrons in its nucleus." What two terms relating to quantity of matter are illustrated by this statement?

8. Where X is a number equal to the formula mass of a substance, complete the following formula: Mass of a mole of a substance = _____.

9. Fill in the blanks in the table below:

Substance	Formula unit	Formula mass	Mass of 1 mole	Numbers and kinds of individual entities in 1 mole
Neon	Ne atom	_____	_____ g	_____ Ne atoms
Nitrogen gas	N_2 molecule	_____	_____ g	_____ N_2 molecules _____ N atoms
Ethene	C_2H_4 molecules	_____	_____ g	_____ C_2H_4 molecules _____ C atoms _____ H atoms

Section 2.4. Physical Properties of Matter

10. Calculate the density of each of the following sustances, for which the mass of a specified volume is given:

 (a) 93.6 g occupying 15 mL
 (b) 0.992 g occupying 1,005 mL
 (c) 13.7 g occupying 11.4 mL
 (d) 16.8 g occupying 3.19 mL

11. Calculate the volume in mL occupied by 156.3 g of water at 4˚C.

12. From densities given in Table 2.3, calculate each of the following:

 (a) Volume of 105 g of iron
 (b) Mass of 157 cm^3 of benzene
 (c) Volume of 1,932 g of air
 (d) Mass of 0.525 cm^3 of carbon tetrachloride
 (e) Volume of 10.0 g of helium
 (f) Mass of 13.2 cm^3 of sugar

13. From information given in Table 2.3, calculate the specific gravities of (a) benzene, (b) carbon tetrachloride, and (c) sulfuric acid relative to water at 4˚C.

14. From information given in this chapter, calculate the density of pure nitrogen gas, N_2, at STP. To do so will require some knowledge of the mole and of the gas laws.

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15. Different colors are due to different _____ of light.

Section 2.5. States of Matter

16. Explain how the various forms of water observed in the environment illustrate the three states of matter.

Section 2.6. Gases

17. Match each gas law stated on the left, below, with the phenomenon that it explains on the right:

A. Charles' law	1. The volume of a mole of ideal gas at STP is 22.4 L.
B. General gas law	2. Tripling the number of moles of gas at constant temperature and pressure triples the volume.
C. Boyle's law	
D. Avogadro's law	3. Raising the absolute temperature of a quantity of gas at constant pressure from 300 K to 450 K increases the gas volume by 50%.
	4. Doubling the pressure on a quantity of gas at constant temperature halves the volume.

18. How might an individual molecule of a gas describe its surroundings? What might it see, feel, and do?

19. Explain pressure and diffusion in terms of the behavior of gas molecules.

20. Use the gas law to calculate whether the volume of a mole of water vapor at 100˚C and 1 atm pressure is 30,600 mL as stated in this chapter.

21. Using the appropriate gas laws, calculate the quantities denoted by the blanks in the table below:

Conditions before				Conditions after			
n_1, mol	V_1, L	P_1, atm	T_1, K	n_2, mol	V_2, L	P_2, atm	T_2, K
1.25	13.2	1.27	298	1.25	(a) _____	0.987	298
1.25	13.2	1.27	298	1.25	(b) _____	1.27	407
1.25	13.2	1.27	298	4.00	(c) _____	1.27	298
1.25	13.2	1.27	298	1.36	(d) _____	1.06	372
1.25	13.2	1.27	298	1.25	30.5	(e) _____	298

Chapter 2.7. Liquids and Solutions

22. In terms of distances between molecules and movement of molecules relative to each other, distinguish between liquids and gases and liquids and solids. Compare and explain shape and compressibility of gases, liquids, and solids.

23. Define (a) evaporation, (b) condensation, (c) vapor pressure as related to liquids.

24. Define (a) solvent, (b) solute, (c) solubility, (d) saturated solution, (e)

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unsaturated solution, (f) insoluble solute.

25. From information given in Section 2.7, calculate the molar concentration of O_2 in water saturated with air at 25˚C

26. Calculate the molar concentration of solute in each of the following solutions:

 (a) Exactly 7.59 g of NH_3 dissolved in 1.500 L of solution.

 (b) Exactly 0.291 g of H_2SO_4 dissolved in 8.65 L of solution.

 (c) Exactly 85.2 g of NaOH dissolved in 5.00 L of solution.

 (d) Exactly 31.25 g of NaCl dissolved in 2.00 L of solution.

 (e) Exactly 6.00 mg of atmospheric N_2 dissolved in water in a total solution volume of 2.00 L.

 (f) Exactly 1,000 g of ethylene glycol, $C_2H_6O_2$ dissolved in water and made up to a volume of 2.00 L.

Section 2.8. Solids

27. Why is the solid state called the most organized form of matter?

28. As related to solids, define (a) sublimation, (b) crystalline solids, and (c) amorphous solids.

Section 2.9. Thermal Properties

29. Experimentally, how could a chemist be sure that (a) a melting point temperature was being observed, (c) the melting point observed was that of a pure substance, and (c) the melting point observed was that of a mixture.

30. Calculate the specific heat of substances for which

 (a) 22.5 J of heat energy was required to raise the temperature of 2.60 g of the substance from 11.5 to 16.2˚C

 (b) 45.6 J of heat energy was required to raise the temperature of 1.90 g of the substance from 8.6 to 19.3˚C

 (c) 1.20 J of heat energy was required to raise the temperature of 3.00 g of the substance from 25.013 to 25.362˚C

31. Calculate the amount of heat required to raise the temperature of 7.25 g of liquid water from 22.7˚C to 29.2˚C.

32. Distinguish between specific heat and (a) heat of vaporization and (b) heat of fusion.

33. Calculate the heat, q, (a) required to evaporate 5.20 g of liquid water and (b) released when 6.50 g of water vapor condenses.

34. Calculate the heat, q, (a) required to melt 5.20 g of ice and (b) released when

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6.50 g of liquid water freezes.

Section 2.10. Separation and Characterization of Matter

35. Suppose that salt were removed from seawater by distillation. In reference to the apparatus shown in Figure 2.11, explain where the pure water product would be isolated and where the salt would be found.

36. How does fractional distillation differ from simple distillation?

37. What are distillation bottoms and what do they have to do in some cases with wastes?

38. Describe solvent extraction as an example of a phase transfer process.

39. For what kind of treatment process is activated carbon used?

40. Name and describe a purification process that operates by virtue of "a membrane that is selectively permeable to water and excludes ionic solutes."

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Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

3 ATOMS AND ELEMENTS

3.1 ATOMS AND ELEMENTS

At the very beginning of this book, chemistry was defined as the science of matter. Chapter 2 examined the nature of matter, largely at a macroscopic level and primarily through its physical properties. Today, the learning of chemistry is simplified by taking advantage of what is known about matter at its most microscopic and fundamental level—atoms and molecules. Although atoms have been viewed so far in this book as simple, indivisible particles, they are in fact complicated bodies. Subtle differences in the arrangements and energies of electrons that make up most of the volume of atoms determine the chemical characteristics of the atoms. In particular, the electronic structures of atoms cause the periodic behavior of the elements, as described briefly in Section 1.3 and summarized in the periodic table in Figure 1.3. This chapter addresses atomic theory and atomic structure in more detail to provide a basis for the understanding of chemistry.

3.2 THE ATOMIC THEORY

The nature of atoms in relation to chemical behavior is summarized in the **atomic theory**. This theory in essentially its modern form was advanced in 1808 by John Dalton, an English schoolteacher, taking advantage of a substantial body of chemical knowledge and the contributions of others. It has done more than any other concept to place chemistry on a sound, systematic theoretical foundation. Those parts of Dalton's atomic theory that are consistent with current understanding of atoms are summarized in Figure 3.1.

Laws that are Explained by Dalton's Atomic Theory

The atomic theory outlined in Figure 3.1 explains the following three laws that are of fundamental importance in chemistry:

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1. **Law of Conservation of Mass**: *There is no detectable change in mass in an ordinary chemical reaction.* (This law was first stated in 1798 by "the father of chemistry," the Frenchman Antoine Lavoisier. Since, as shown in Item 5 of Figure 3.1, no atoms are lost, gained, or changed in chemical reactions, mass is conserved.)

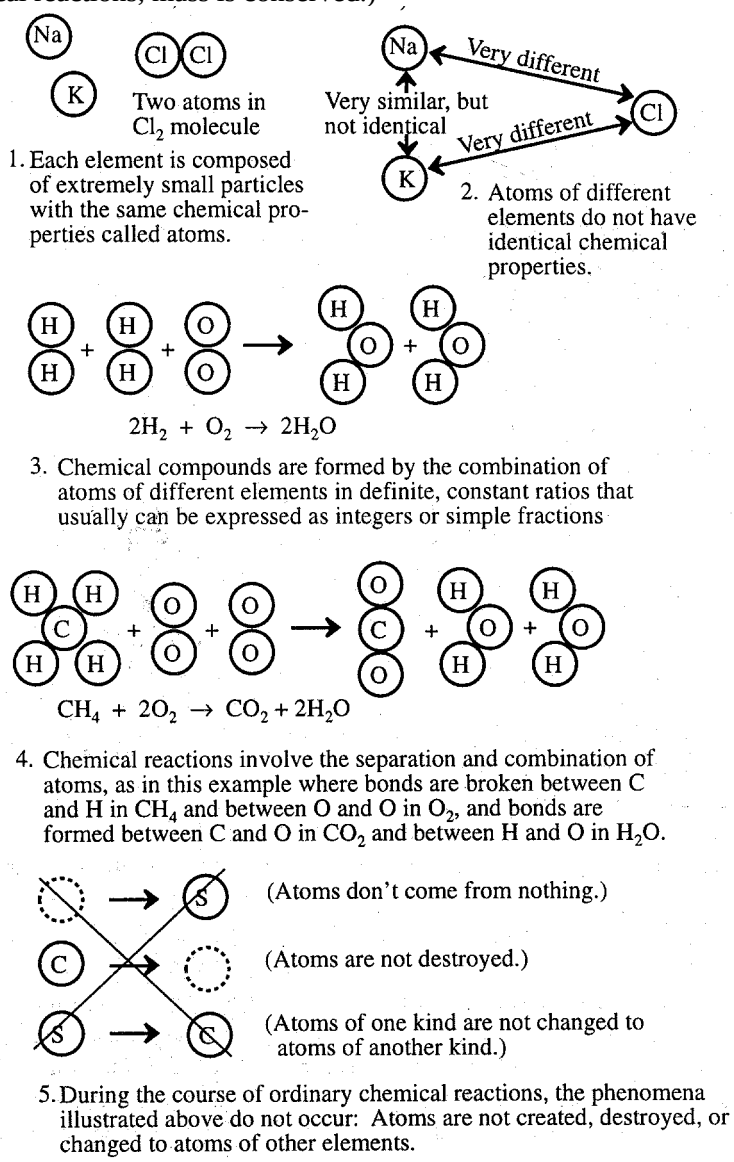


Figure 3.1 Illustration of Dalton's atomic theory.

2. **Law of Constant Composition**: *A specific chemical compound always contains the same elements in the same proportions by mass.* (If atoms always combine in definite, constant ratios to form a particular chemical compound, as implied in Item 3 of Figure 3.1, the elemental composition of the compound by mass always remains the same.)

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3. **Law of Multiple Proportions**: *When two elements combine to form two or more compounds, the masses of one combining with a fixed mass of the other are in ratios of small whole numbers* (as illustrated for two compounds composed only of carbon and hydrogen below).

 For CH_4: Relative mass of hydrogen = 4 × 1.0 = 4.0 (because there are 4 atoms of H, atomic mass 1.0)

 Relative mass of carbon = 1 × 12.0 = 12.0 (because there is 1 atom of C, atomic mass 12.0)

 $$\text{C/H ratio for } CH_4 = \frac{\text{Mass of C}}{\text{Mass of H}} = \frac{12.0}{4.0} = 3.0$$

 For C_2H_6: Relative mass of hydrogen = 6 × 1.0 = 6.0 (because there are 6 atoms of H, atomic mass 1.0)

 Relative mass of carbon = 2 × 12.0 = 24.0 (because there are 2 atoms of C, atomic mass 12.0)

 $$\text{C/H ratio for } C_2H_6 = \frac{\text{Mass of C}}{\text{Mass of H}} = \frac{24.0}{6.0} = 4.0$$

 Comparing C_2H_6 and CH_4: $$\frac{\text{C/H ratio for } C_2H_6}{\text{C/H ratio for } CH_4} = \frac{4.0}{3.0} = 4/3$$

 Note that this is a ratio of small whole numbers.

Small Size of Atoms

It is difficult to imagine just how small an individual atom is. An especially small unit of mass, the *atomic mass unit*, *u*, is used to express the masses of atoms. This unit was defined in Section 1.3 as a mass equal to exactly 1/12 that of the carbon-12 isotope. An atomic mass unit is only 1.66×10^{-24} g. An average atom of hydrogen, the lightest element, has a mass of only 1.0079 u. The average mass of an atom of uranium, the heaviest naturally occurring element, is 238.03 u. To place these values in perspective, consider that a signature written by ballpoint pen on a piece of paper typically has a mass of 0.1 mg (1×10^{-4} g). This mass is equal to 6×10^{19} u. It would take almost 60 000 000 000 000 000 000 hydrogen atoms to equal the mass of ink in such a signature!

Atoms visualized as spheres have diameters of around $1\text{-}3 \times 10^{-10}$ meters (100-300 picometers, pm). By way of comparison, a small marble has a diameter of around 1 cm (1×10^{-2} m), which is about 100 000 000 times that of a typical atom.

Atomic Mass

As defined in Section 1.3, the *atomic mass* of an element is the average mass of all atoms of the element relative to carbon-12 taken as exactly 12. Since atomic masses are *relative* quantities, they can be expressed without units. Or atomic masses may be given in atomic mass units. For example, an atomic mass of 14.0067 for nitrogen means that the average mass of all nitrogen atoms is 14.0067/12 as great as the mass of the carbon-12 isotope and is also 14.0067 u.

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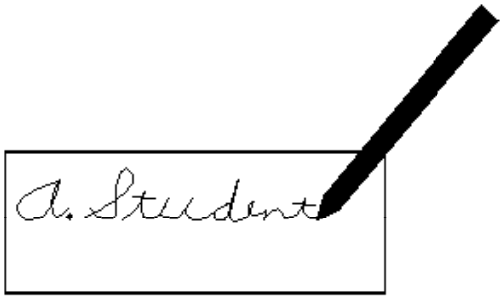


Figure 3.2 The ballpoint pen ink in a typical signature might have a mass of 6 x 10^{19} u.

3.3 SUBATOMIC PARTICLES

Small as atoms are, they in turn consist of even smaller entities called **subatomic particles**. Although physicists have found several dozen of these, chemists need consider only three—*protons*, *neutrons*, and *electrons* (these were introduced briefly in Section 1.3). These subatomic particles differ in mass and charge. Like the atom, their masses are expressed in atomic mass units.

The proton, *p*, has a mass of 1.007277 u and a unit charge of +1. This charge is equal to 1.6022×10^{-19} coulombs, where a coulomb is the amount of electrical charge involved in a flow of electrical current of 1 ampere for 1 second.

The neutron, *n*, has no electrical charge and a mass of 1.009665 u. The proton and neutron each have a mass of essentially 1 u and are said to have a *mass number* of 1. (Mass number is a useful concept expressing the total number of protons and neutrons, as well as the approximate mass, of a nucleus or subatomic particle.)

The electron, *e*, has an electrical charge of -1. It is very light, however, with a mass of only 0.00054859 u, about 1/1840 that of the proton or neutron. Its mass number is 0. The properties of protons, neutrons, and electrons are summarized in Table 3.1.

Table 3.1 Properties of Protons, Neutrons, and Electrons

Subatomic particle	Symbol[1]	Unit charge	Mass number	Mass in μ	Mass in grams
Proton	*p*	+1	1	1.007277	1.6726 x 10^{-24}
Neutron	*n*	0	1	1.008665	1.6749 x 10^{-24}
Electron	*e*	-1	0	0.000549	9.1096 x 10^{-28}

[1] The mass number and charge of each of these kinds of particles can be indicated by a superscript and subscript, respectively in the symbols ${}_{1}^{1}p$, ${}_{0}^{1}n$, ${}_{-1}^{0}e$.

Although it is convenient to think of the proton and neutron as having the same mass, and each is assigned a mass number of 1, it is seen in Table 3.1 that their exact masses differ slightly from each other. Furthermore, the mass of an atom differs slightly from the sum of the masses of subatomic particles composing the atom. This is because of the energy relationships involved in holding the subatomic particles

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together in atoms so that the masses of the atom's constituent subatomic particles do not add up to exactly the mass of the atom.

3.4 THE BASIC STRUCTURE OF THE ATOM

As mentioned in Section 1.3, protons and neutrons are located in the *nucleus* of an atom; the remainder of the atom consists of a cloud of rapidly moving electrons. Since protons and neutrons have much higher masses than electrons, essentially all the mass of an atom is in its nucleus. However, the electron cloud makes up virtually all of the volume of the atom, and the nucleus is very small.

Atomic Number, Isotopes, and Mass Number of Isotopes

All atoms of the same element have the same number of protons and electrons equal to the *atomic number* of the element. (When reference is made to atoms here it is understood that they are electrically neutral atoms and not ions consisting of atoms that have lost or gained 1 or more electrons.) Thus, all helium atoms have 2 protons in their nuclei, and all nitrogen atoms have 7 protons.

In Section 1.3, *isotopes* were defined as atoms of the same element that differ in the number of neutrons in their nuclei. It was noted in Section 3.3 that both the proton and neutron have a *mass number* of exactly l. Mass number is commonly used to denote isotopes. The **mass number of an isotope** *is the sum of the number of protons and neutrons in the nucleus of the isotope.* Since atoms with the same number of protons—that is, atoms of the same element—may have different numbers of neutrons, several isotopes may exist of a particular element. The naturally occurring forms of some elements consist of only one isotope, but isotopes of these elements can be made artificially, usually by exposing the elements to neutrons produced by a nuclear reactor.

It is convenient to have a symbol that clearly designates an isotope of an element. Borrowing from nuclear science, a superscript in front of the symbol for the element is used to show the mass number and a subscript before the symbol designates the number of protons in the nucleus (atomic number). Using this notation denotes carbon-12 as $^{12}_{6}C$.

Exercise: Fill in the blanks designated with letters in the table below:

Element	Atomic number	Mass number of isotope	Number of neutrons in nucleus	Isotope symbol
Nitrogen	7	14	7	$^{14}_{7}N$
Chlorine	17	35	(a)_____	$^{35}_{17}N$
Chlorine	(b)_____	37	(c)_____	(d)_____
(e)_____	6	(f)_____	7	(g)_____
(h)_____	(i)_____	(j)_____	(k)_____	$^{11}_{5}B$

Answers: (a) 18, (b) 17, (c) 20, (d) $^{37}_{17}Cl$, (e) carbon, (f) 13, (g) $^{13}_{6}C$, (h) boron, (i) 5, (j) 11, (k) 6

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Electrons in Atoms

In Section 1.3, electrons around the nucleus of an atom were depicted as forming a cloud of negative charge. The energy levels, orientations in space, and behavior of electrons vary with the number of them contained in an atom. In a general sense, the arrangements of electrons in atoms are described by *electron configuration*, a term discussed in some detail later in this chapter.

Attraction between Electrons and the Nucleus

The electrons in an atom are held around the nucleus by the attraction between their negative charges and the positive charges of the protons in the nucleus. Opposite electrical charges attract, and like charges repel. The forces of attraction and repulsion are expressed quantitatively by **Coulomb's law**,

$$F = \frac{Q_1 Q_2}{d} \qquad (3.4.1)$$

where F is the force of interaction, Q_1 and Q_2 are the electrical charges on the bodies involved, and d is the distance between the bodies.

Coulomb's law explains the attraction between negatively charged electrons and the positively charged nucleus in an atom. However, the law does not explain why electrons move around the nucleus, rather than coming to rest on it. The behavior of electrons in atoms—as well as the numbers, types, and strengths of chemical bonds formed between atoms—is explained by *quantum theory*, a concept that is discussed in some detail in Sections 3.11-3.16.

3.5 DEVELOPMENT OF THE PERIODIC TABLE

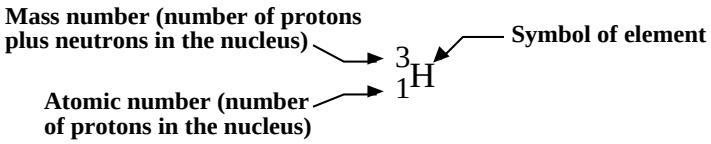
The *periodic table*, which was mentioned briefly in connection with the elements in Section 1.3, was first described by the Russian chemist Dmitri Mendeleev in 1867. It was based upon Mendeleev's observations of periodicity in chemical behavior without any knowledge of atomic structure. The periodic table is discussed in more detail in this chapter along with the development of the concepts of atomic structure. Elements are listed in the periodic table in an ordered, systematic way that correlates with their electron structures. The elements are placed in rows or **periods** of the periodic table in order of increasing atomic number such that there is a periodic repetition of elemental properties across the periods. The rows are arranged such that elements in vertical columns called **groups** have similar chemical properties reflecting similar arrangements of the outermost electrons in their atoms.

With some knowledge of the ways that electrons behave in atoms it is much easier to develop the concept of the periodic table. This is done for the first 20 elements in the following sections. After these elements are discussed, they can be placed in an abbreviated 20-element version of the periodic table. Such a table is shown in Figure 3.9.

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3.6 HYDROGEN, THE SIMPLEST ATOM

The simplest atom is that of **hydrogen**, as it has only one positively charged proton in its nucleus, that is surrounded by a cloud of negative charge formed by only one electron. By far the most abundant kind of hydrogen atom has no neutrons in its nucleus. Having only one proton with a mass number (see Section 3.3) of 1, and 1 electron with a mass number of zero, the mass number of this form of hydrogen is 1 + 0 = 1. There are, however, two other forms of hydrogen atoms having, in addition to the proton, 1 and 2 neutrons, respectively, in their nuclei. The three different forms of elemental hydrogen are *isotopes* of hydrogen that all have the same number of protons, but different numbers of neutrons in their nuclei. Only about 1 of 7000 hydrogen atoms is ${}_{1}^{2}\mathrm{H}$, deuterium, mass number 2 (from 1 proton + 1 neutron). The mass number of *tritium*, which has 2 neutrons, is 1 (from 1 proton + 2 neutrons) = 3. These three forms of hydrogen atoms can be designated as ${}_{1}^{1}\mathrm{H}$, ${}_{1}^{2}\mathrm{H}$, and ${}_{1}^{3}\mathrm{H}$. The meaning of this notation is reviewed below:



Designation of Hydrogen in the Periodic Table

The atomic mass of hydrogen is 1.0079. This means that the average atom of hydrogen has a mass of 1.0079 u (atomic mass units); hydrogen's atomic mass is simply 1.0079 relative to the carbon-12 isotope taken as exactly 12. With this information it is possible to place hydrogen in the periodic table with the designation shown in Figure 3.3.

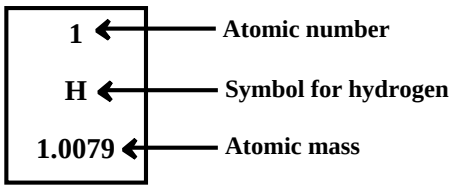


Figure 3.3 Designation of hydrogen in the periodic table.

Showing Electrons in Hydrogen Atoms and Molecules

It is useful to have some simple way of showing the hydrogen atom's single electron in chemical symbols and formulas. This is accomplished with **electron-dot symbols** or **Lewis symbols** (after G. N. Lewis), which use dots around the symbol of an element to show outer electrons (those that may become involved in chemical bonds). The Lewis symbol for hydrogen is



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As mentioned in Section 1.3, elemental hydrogen consists of molecules made up of 2 H atoms held together by a chemical bond consisting of two shared electrons. Just as it is useful to show electrons in atoms with a Lewis symbol, it is helpful to visualize molecules and the electrons in them with **electron-dot formulas** or **Lewis formulas** as shown for the H_2 molecule in Figure 3.4.

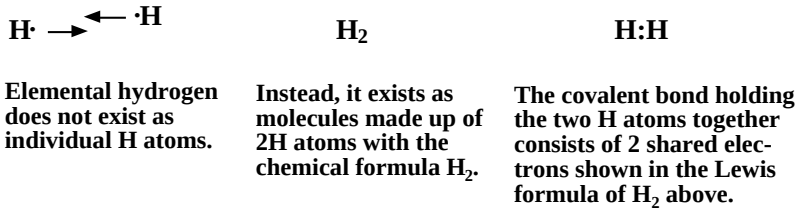


Figure 3.4. Lewis formula for hydrogen molecules.

Properties of Elemental Hydrogen

Pure hydrogen is colorless and odorless. It is a gas at all but very low temperatures; liquid hydrogen boils at -253˚C and solidifies at -259˚C. Hydrogen gas has the lowest density of any pure substance. It reacts chemically with a large number of elements, and hydrogen-filled balloons that float readily in the atmosphere also explode convincingly when touched with a flame because of the following very rapid reaction with oxygen in the air:

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (3.5.1)$$

Production and Uses of Elemental Hydrogen

Elemental hydrogen is one of the more widely produced industrial chemicals. For use in chemical synthesis and other industrial applications, it is commonly made by **steam reforming** of methane (natural gas, CH_4) under high-temperature, high-pressure conditions:

$$CH_4 + H_2O \xrightarrow[30\ \text{atm P}]{800^\circ\text{C T}} CO + 3H_2 \qquad (3.5.2)$$

Hydrogen is used to manufacture a number of chemicals. One of the most important of these is ammonia, NH_3. Methanol (methyl alcohol, CH_3OH) is a widely used industrial chemical and solvent synthesized by the following reaction between carbon monoxide and hydrogen:

$$CO + 2H_2 \rightarrow CH_3OH \qquad (3.5.3)$$

Methanol made by this process can be blended with gasoline to yield a fuel that produces relatively less pollutant carbon monoxide; such “oxygenated gasoline additives” are now required for use in some cities urban areas. Gasoline is upgraded by the chemical addition of hydrogen to some petroleum fractions. Synthetic petroleum can be made by the addition of hydrogen to coal at high temperatures and

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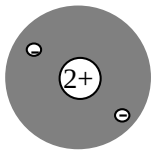
pressures. A widely used process in the food industry is the addition of hydrogen to unsaturated vegetable oils in the synthesis of margarine and other hydrogenated fats and oils.

3.7 HELIUM, THE FIRST ATOM WITH A FILLED ELECTRON SHELL

In Section 3.4 it was mentioned that the *electron configurations* of atoms determine their chemical behavior. Electrons in atoms occupy distinct *energy levels*. At this point, it is useful to introduce the concept of the **electron shell** to help explain electron energy levels and their influence on chemical behavior. Each electron shell can hold a maximum number of electrons. An atom with a **filled electron shell** is especially content in a chemical sense, with little or no tendency to lose, gain, or share electrons. Elements with these characteristics exist as gas-phase atoms and are called *noble gases*. The high stability of the noble gas electron configuration is explained in more detail in Section 3.9.

Examined in order of increasing atomic number, the first element consisting of atoms with filled electron shells is helium, He, atomic number 2. All helium atoms contain 2 protons and 2 electrons. Virtually all helium atoms are $^{4}_{2}$He that contain 2 neutrons in their nuclei; the $^{3}_{2}$He isotope containing only 1 neutron in its nucleus occurs to a very small extent. The atomic mass of helium is 4.00260.

The two electrons in the helium atom are shown by the Lewis symbol illustrated in Figure 3.5. These electrons constitute a *filled electron shell*, so that helium is a *noble gas* composed of individual helium atoms that have no tendency to form chemical bonds with other atoms. Helium gas has a very low density of only 0.164 g/L at 25˚C and 1 atm pressure.



A helium atom has a filled electron shell containing 2 electrons.

He:

It can be represented by the Lewis symbol above.

Figure 3.5. Two representations of the helium atom having a filled electron shell

Occurrence and Uses of Helium

Helium is extracted from some natural gas sources that contain up to 10% helium by volume. It has many uses that depend upon its unique properties. Because of its very low density compared to air, helium is used to fill weather balloons and airships. Helium is non-toxic, odorless, tasteless, and colorless. Because of these properties and its low solubility in blood, helium is mixed with oxygen for breathing by deep sea divers and persons with some respiratory ailments. Use of helium by divers avoids the very painful condition called “the bends” caused by bubbles of nitrogen forming from nitrogen gas dissolved in blood.

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Liquid helium, which boils at a temperature of only 4.2 K above absolute zero is especially useful in the growing science of **cryogenics**, which deals with very low temperatures. Some metals are superconductors at such temperatures so that helium is used to cool electromagnets that develop very powerful magnetic fields for a relatively small magnet. Such magnets are components of the very useful chemical tool known as nuclear magnetic resonance (NMR). The same kind of instrument modified for clinical applications and called MRI is used as a medical diagnostic tool.

3.8 LITHIUM, THE FIRST ATOM WITH BOTH INNER AND OUTER ELECTRONS

The third element in the periodic table is lithium (Li), atomic number 3, atomic mass 6.941. The most abundant lithium isotope has 4 neutrons in its nucleus, so it has a mass number of 7 and is designated $^{7}_{3}$Li. A less common isotope, $^{6}_{3}$Li has only 3 neutrons.

Lithium is the first element in the periodic table that is a *metal*. Mentioned in Section 2.2, metals tend to have the following properties:

- Characteristic **luster** (like freshly-polished silverware or a new penny)
- **Malleable** (can be pounded or pressed into various shapes without breaking)
- **Conduct electricity**
- Chemically, tend to **lose electrons** and form cations (see Section 1.4) with charges of +1 to +3.

Lithium is the lightest metal with a density of only 0.531 g/cm^3.

Uses of Lithium

Lithium compounds have a number of important uses in industry and medicine. Lithium carbonate, Li_2CO_3, is one of the most important lithium compounds and is used as the starting material for the manufacture of many other lithium compounds. It is an ingredient of specialty glasses, enamels, and specialty ceramic ware having low thermal expansion coefficients (minimum expansion when heated). Lithium carbonate is widely prescribed as a drug to treat acute mania in manic-depressive and schizo-affective mental disorders. Lithium hydroxide, LiOH, is an ingredient in the manufacture of lubricant greases and in some long-life alkaline storage batteries.

The lithium atom has three electrons. As shown in Figure 3.6, lithium has both **inner electrons**—in this case 2 contained in an **inner shell**—as in the immediately preceding noble gas helium, and an **outer electron** that is farther from, and less strongly attracted to, the nucleus. The outer electron is said to be in the atom's **outer shell**. The inner electrons are, on the average, closer to the nucleus than is the outer electron, are very difficult to remove from the atom, and do not become involved in chemical bonds. Lithium's outer electron is relatively easy to remove from the atom, which is what happens when ionic bonds involving Li^+ ion are formed (see Section

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1.4). The distinction between inner and outer electrons is developed to a greater extent later in this chapter.

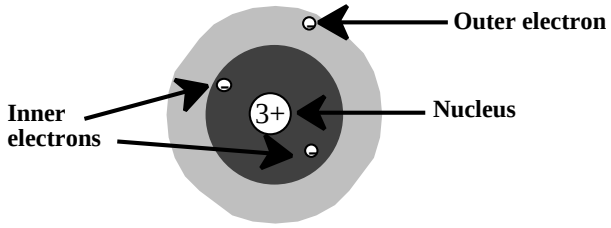


Figure 3.6 An atom of lithium, Li, has 2 inner electrons and 1 outer electron. The latter can be lost to another atom to produce the Li^+ ion, which is present in ionic compounds (see Section 1.4).

In atoms such as lithium that have both outer and inner electrons, the Lewis symbol shows only the outer electrons. Therefore, the Lewis symbol of lithium is

$$Li\cdot$$

A lithium atom's loss of its single outer electron is shown by the **half-reaction** (one in which there is a net number of electrons on either the reactant or product side) in Figure 3.7. The Li^+ product of this reaction has the very stable helium core of 2 electrons. The Li^+ ion is a constituent of ionic lithium compounds in which it is held by attraction for negatively charged anions (such as Cl^-) in the crystalline lattice of the ionic compound. The tendency to lose its outer electron and to be stabilized in ionic compounds determines lithium's chemical behavior.

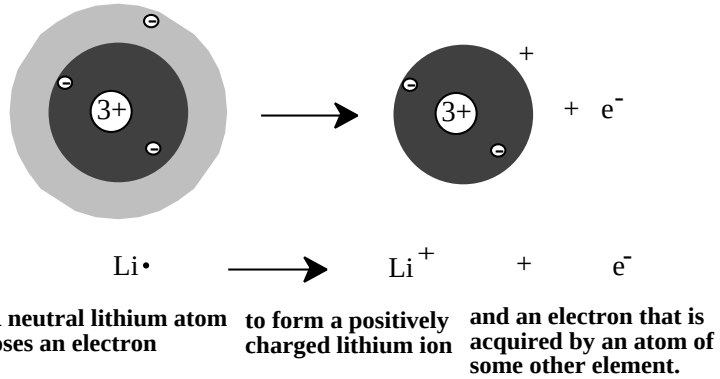


Figure 3.7. Half-reaction showing the formation of Li^+ from an Li atom. The Li^+ ion has the especially stable helium core of just 2 electrons. The atom to which the electron is lost is not shown, so this is a half-reaction.

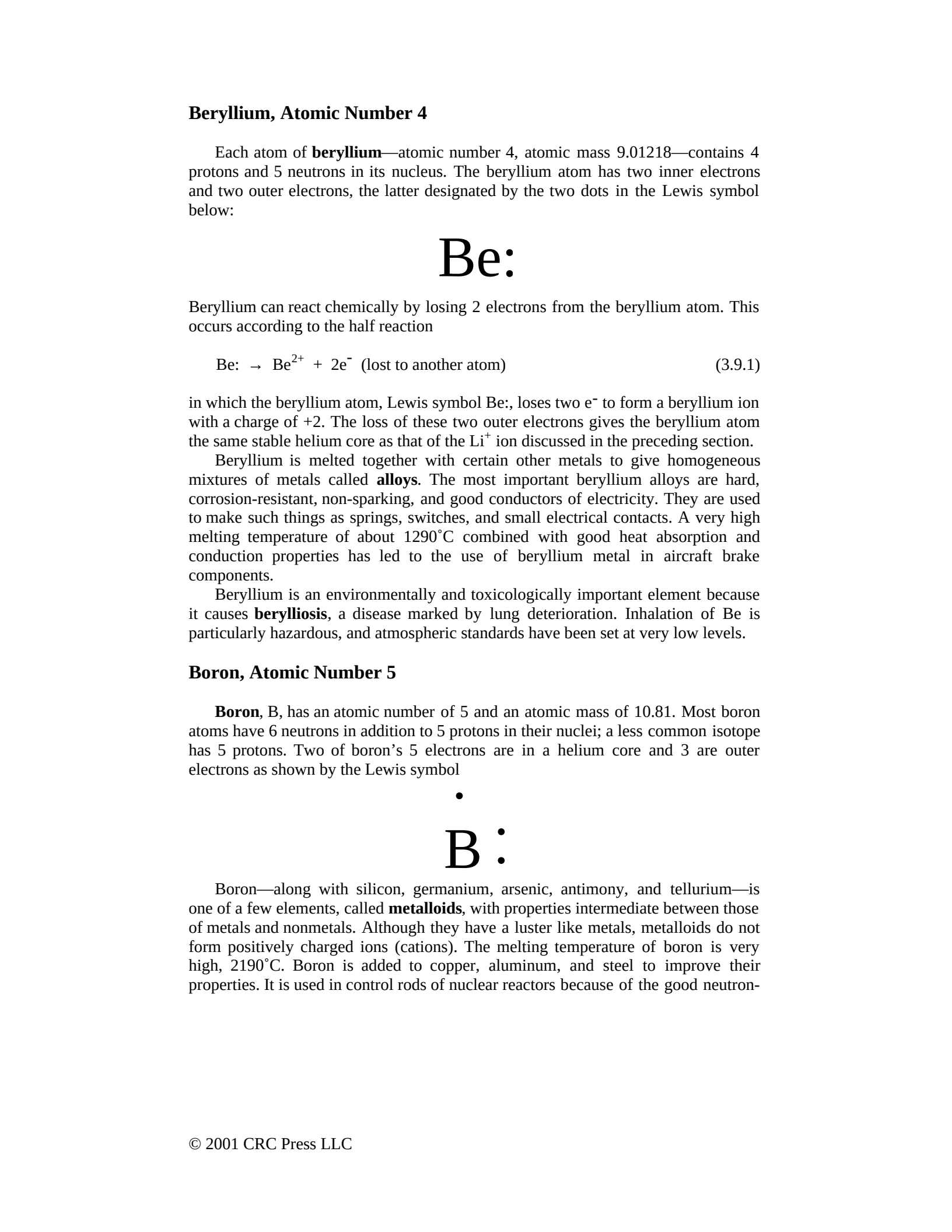
3.9 THE SECOND PERIOD, ELEMENTS 4-10

In this section, elements 4-10 will be discussed and placed in the periodic table to complete a period in the table.

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Beryllium, Atomic Number 4

Each atom of **beryllium**—atomic number 4, atomic mass 9.01218—contains 4 protons and 5 neutrons in its nucleus. The beryllium atom has two inner electrons and two outer electrons, the latter designated by the two dots in the Lewis symbol below:



Beryllium can react chemically by losing 2 electrons from the beryllium atom. This occurs according to the half reaction

$$\text{Be:} \rightarrow \text{Be}^{2+} + 2e^{-} \text{ (lost to another atom)} \qquad (3.9.1)$$

in which the beryllium atom, Lewis symbol Be:, loses two e^- to form a beryllium ion with a charge of +2. The loss of these two outer electrons gives the beryllium atom the same stable helium core as that of the Li^+ ion discussed in the preceding section.

Beryllium is melted together with certain other metals to give homogeneous mixtures of metals called **alloys**. The most important beryllium alloys are hard, corrosion-resistant, non-sparking, and good conductors of electricity. They are used to make such things as springs, switches, and small electrical contacts. A very high melting temperature of about 1290˚C combined with good heat absorption and conduction properties has led to the use of beryllium metal in aircraft brake components.

Beryllium is an environmentally and toxicologically important element because it causes **berylliosis**, a disease marked by lung deterioration. Inhalation of Be is particularly hazardous, and atmospheric standards have been set at very low levels.

Boron, Atomic Number 5

Boron, B, has an atomic number of 5 and an atomic mass of 10.81. Most boron atoms have 6 neutrons in addition to 5 protons in their nuclei; a less common isotope has 5 protons. Two of boron's 5 electrons are in a helium core and 3 are outer electrons as shown by the Lewis symbol

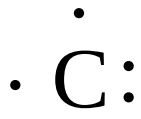
Boron—along with silicon, germanium, arsenic, antimony, and tellurium—is one of a few elements, called **metalloids**, with properties intermediate between those of metals and nonmetals. Although they have a luster like metals, metalloids do not form positively charged ions (cations). The melting temperature of boron is very high, 2190˚C. Boron is added to copper, aluminum, and steel to improve their properties. It is used in control rods of nuclear reactors because of the good neutron-

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absorbing properties of the $^{10}_{5}B$ isotope. Some chemical compounds of boron, especially boron nitride, BN, are noted for their hardness. Boric acid, H_3BO_3, is used as a flame retardant in cellulose insulation in houses. The oxide of boron, B_2O_3, is an ingredient of fiberglass, used in textiles and insulation.

Carbon, Atomic Number 6

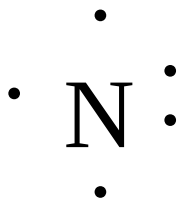
Atoms of **carbon**, C, have 2 inner and 4 outer electrons, the latter shown by the Lewis symbol



The carbon-12 isotope with 6 protons and 6 neutrons in its nucleus, $^{12}_{6}C$ constitutes 98.9% of all naturally occurring carbon. The $^{13}_{6}C$ isotope makes up 1.1% of all carbon atoms. As discussed in Chapter 25, radioactive carbon-14, $^{14}_{6}C$, is present in some carbon sources.

Carbon is an extremely important element with unique chemical properties without which life could not exist. All of organic chemistry (Chapter 10) is based upon compounds of carbon, and it is an essential element in life molecules (studied as part of biochemistry, Chapter 11). Carbon atoms are able to bond to each other to form long straight chains, branched chains, rings, and three-dimensional structures. As a result of its self-bonding abilities, carbon exists in several elemental forms. These include powdery carbon black; very hard, clear diamonds; and graphite so soft that it is used as a lubricant. Activated carbon prepared by treating carbon with air, carbon dioxide, or steam at high temperatures is widely used to absorb undesirable pollutant substances from air and water. Carbon fiber has been developed as a structural material in the form of composites consisting of strong strands of carbon bonded together with special plastics and epoxy resins.

Nitrogen, N, composes 78% by volume of air in the form of diatomic N_2 molecules. The atomic mass of nitrogen is 14.0067, and the nuclei of N atoms contain 7 protons and 7 neutrons. Nitrogen has 5 outer electrons, so its Lewis symbol is



Like carbon, nitrogen is a nonmetal. Pure N_2 is prepared by distilling liquified air, and it has a number of uses. Since nitrogen gas is not very chemically reactive, it is used as an inert atmosphere in some industrial applications, particularly where fire or chemical reactivity may be a hazard. People have been killed by accidentally entering chambers filled with nitrogen gas, which acts as a simple asphyxiant with no odor to warn of its presence. Liquid nitrogen boils at a very cold -190˚C. It is widely used to maintain very low temperatures in the laboratory, for quick-freezing

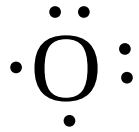
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foods, and in freeze-drying processes. Freeze-drying is used to isolate fragile biochemical compounds from water solution, for the concentration of environmental samples to be analyzed for pollutants, and for the preparation of instant coffee and other dehydrated foods. It has potential applications in the concentration and isolation of hazardous waste substances.

Like carbon, nitrogen is an essential element for life processes. Nitrogen is an ingredient of all of the amino acids found in proteins. Nitrogen compounds are fertilizers essential for the growth of plants. The **nitrogen cycle**, which involves incorporation of N_2 from the atmosphere into living matter and chemically bound nitrogen in soil and water, then back into the atmosphere again, is one of nature's fundamental cycles. Nitrogen compounds, particularly ammonia (NH_3), and nitric acid (HNO_3), are widely used industrial chemicals.

Oxygen, Atomic Number 8

Like carbon and nitrogen, **oxygen**, atomic number 8, is a major component of living organisms. Oxygen is a nonmetal existing as molecules of O_2 in the elemental gas state, and air is 21% oxygen by volume. Like all animals, humans require oxygen to breathe and to maintain their life processes. The nuclei of oxygen atoms contain 8 protons and 8 neutrons, and the atomic mass of oxygen is 15.9994. The oxygen atom has 6 outer electrons, as shown by its Lewis symbol below:



In addition to O_2, there are two other important elemental oxygen species in the atmosphere. These are atomic oxygen, O, and ozone, O_3. These species are normal constituents of the stratosphere, a region of the atmosphere that extends from about 11 kilometers to about 50 km in altitude. Oxygen atoms are formed when high-energy ultraviolet radiation strikes oxygen molecules high in the stratosphere:

$$O_2 \xrightarrow[\text{radiation}]{\text{Ultraviolet}} O + O \tag{3.9.3}$$

The oxygen atoms formed by the above reaction combine with O_2 molecules,

$$O + O_2 \rightarrow O_3 \tag{3.9.4}$$

to form ozone molecules. These molecules make up the **ozone layer** in the stratosphere and effectively absorb additional high-energy ultraviolet radiation. If it weren't for this phenomenon, the ultraviolet radiation would reach the Earth's surface and cause painful sunburn and skin cancer in exposed people. However, ozone produced in photochemical smog at ground level is toxic to animals and plants.

The most notable chemical characteristic of elemental oxygen is its tendency to combine with other elements in energy-yielding reactions. Such reactions provide

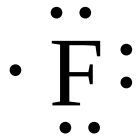
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the energy that propels automobiles, heats buildings, and keeps body processes going. One of the most widely used chemical reactions of oxygen is that with hydrocarbons, particularly those from petroleum and natural gas. For example, butane (C_4H_{10}, a liquifiable gaseous hydrocarbon fuel) burns in oxygen from the atmosphere, a reaction that provides heat in home furnaces, water heaters, and other applications:

$$2C_4H_{10} + 13O_2 \rightarrow 8CO_2 + 10H_2O \qquad (3.9.5)$$

Fluorine, Atomic Number 9

Fluorine, F, has 7 outer electrons, so its Lewis symbol is



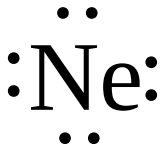
Under ordinary conditions, elemental fluorine is a greenish-yellow gas consisting of F_2 molecules.

Fluorine compounds have many uses. One of the most notable of these is the manufacture of chlorofluorocarbon compounds known by the trade name Freon. These are chemical combinations of chlorine, fluorine, and carbon, an example of which is dichlorodifluoromethane, Cl_2CF_2. These compounds used to be widely employed as refrigerant fluids and blowing agents to make foam plastics; they were once widely used as propellants in aerosol spray cans. Uses of chlorofluorocarbons have now been largely phased out because of their role in destroying stratospheric ozone (discussed with oxygen, above).

Neon, Atomic Number 10

The last element in the period of the periodic table under discussion is **neon**. Air is about 2 parts per thousand neon by volume, and neon is obtained by the distillation of liquid air. Neon is especially noted for its use in illuminated signs that consist of glass tubes containing neon, through which an electrical current is passed, causing the neon gas to emit a characteristic glow.

In addition to 10 protons, most neon atoms have 10 neutrons in their nuclei, although some have 12, and a very small percentage have 11. As shown by its Lewis symbol,

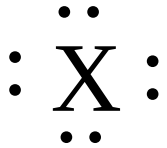


the neon atom has 8 outer electrons, which constitute a *filled electron shell*, just as the 2 electrons in helium give it a filled electron shell. Because of this "satisfied" outer shell, the neon atom has no tendency to acquire, give away, or share electrons. Therefore, neon is a *noble gas*, like helium, and consists of individual neon atoms.

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Stability of the Neon Noble Gas Electron Octet

In going through the rest of the periodic table it can be seen that all other atoms with 8 outer electrons, like neon, are also noted for a high degree of chemical stability. In addition to neon, these noble gases are argon (atomic number 18), krypton (atomic number 36), xenon (atomic number 54), and radon (atomic number 86). Each of these may be represented by the Lewis symbol



where X is the chemical symbol of the noble gas. It is seen that these atoms each have 8 outer electrons, a group known as an **octet** of electrons. In many cases, atoms that do not have an octet of outer electrons acquire one by losing, gaining, or sharing electrons in chemical combination with other atoms; that is, they acquire a **noble gas outer electron configuration**. For all noble gases except helium, which has only 2 electrons, the noble gas outer electron configuration consists of eight electrons. The tendency of elements to acquire an 8-electron outer electron configuration, which is very useful in predicting the nature of chemical bonding and the formulas of compounds that result, is called the **octet rule**. Although the use of the octet rule to explain and predict bonding is discussed in some detail in Chapter 4, at this point it is useful to show how it explains bonding between hydrogen and carbon in methane, as illustrated in Figure 3.8.

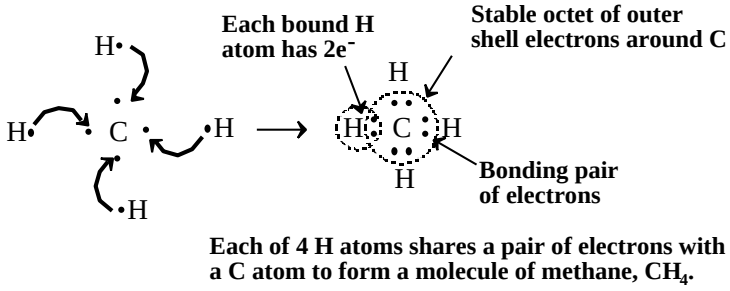


Figure 3.8 Illustration of the octet rule in methane.

3.10 ELEMENTS 11-20, AND BEYOND

The abbreviated version of the periodic table will be finished with elements 11 through 20. The names, symbols, electron configurations, and other pertinent information about these elements are given in Table 3.2. An abbreviated periodic table with these elements in place is shown in Figure 3.9. This table shows the Lewis symbols of all of the elements to emphasize their orderly variation across periods and similarity in groups of the periodic table.

The first 20 elements in the periodic table are very important. They include the three most abundant elements on the earth's surface (oxygen, silicon, aluminum); all

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Table 3.2 Elements 11-20

Atomic number	Name and Lewis symbol	Atomic mass	Number of outer e^-	Major properties and uses
11	Sodium, Na•	22.9898	1	Soft, chemically very reactive metal. Nuclei contain 11 *p* and 12 *n*.
12	Magnesium, Mg:	24.312	2	Lightweight metal used in aircraft components, extension ladders, portable tools. Chemically very reactive. Three isotopes with 12, 13, 14 *n*.
13	Aluminum, Al:	26.9815	3	Lightweight metal used in aircraft, automobiles, electrical transmission line. Chemically reactive, but forms self-protective coating.
14	Silicon, ·Si:	28.086	4	Nonmetal, 2nd most abundant metal in Earth's crust. Rock constituent. Used in semiconductors.
15	Phosphorus, •P:	30.9738	5	Chemically very reactive nonmetal. Highly toxic as elemental white phosphorus. Component of bones and teeth, genetic material (DNA), fertilizers, insecticides.
16	Sulfur, •S:	32.064	6	Brittle, generally yellow nonmetal. Essential nutrient for plants and animals, occurring in amino acids. Used to manufacture sulfuric acid. Present in pollutant sulfur dioxide, SO_2.
17	Chlorine, •Cl:	35.453	7	Greenish-yellow toxic gas composed of molecules of Cl_2· Manufactured in large quantities to disinfect water and to manufacture plastics and solvents.
18	Argon, :Ar:	39.948	8	Noble gas used to fill light bulbs and as a plasma medium in inductively coupled plasma atomic emission analysis of elemental pollutants.
19	Potassium, K•	39.098	1	Chemically reactive alkali metal very similar to sodium in chemical and physical properties. Essential fertilizer for plant growth as K^+ ion.
20	Calcium, Ca:	40.078	2	Chemically reactive alkaline earth metal with properties similar to those of magnesium.

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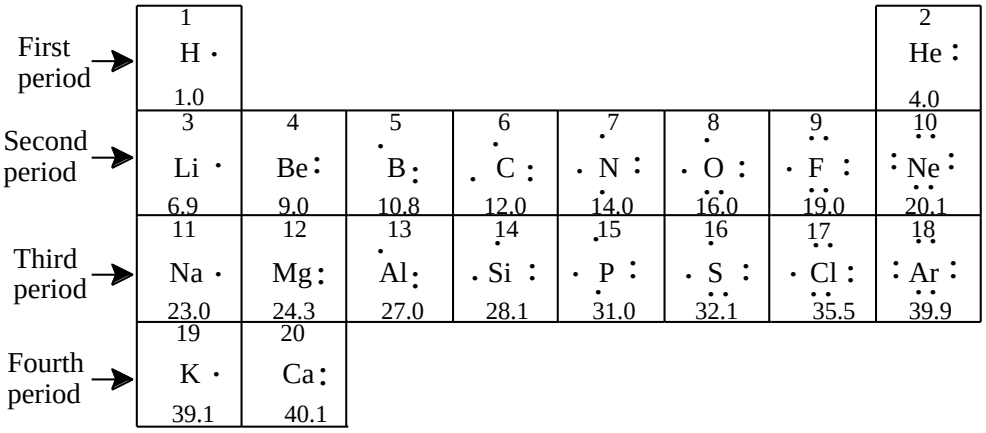


Figure 3.9 Abbreviated 20-element version of the periodic table showing Lewis symbols of the elements

elements of any appreciable significance in the atmosphere (hydrogen in H_2O vapor, N_2, O_2, carbon in CO_2, argon, and neon); the elements making up most of living plant and animal matter (hydrogen, oxygen, carbon, nitrogen, phosphorus, and sulfur); and elements such as sodium, magnesium, potassium, calcium, and chlorine that are essential for life processes. The chemistry of these elements is relatively straightforward and easy to relate to their atomic structures. Therefore, emphasis is placed on them in the earlier chapters of this book. It is helpful to remember their names, symbols, atomic numbers, atomic masses, and Lewis symbols.

As mentioned in Section 1.3, the vertical columns of the table contain *groups* of elements that have similar chemical structures. Hydrogen, H, is an exception and is not regarded as belonging to any particular group because of its unique chemical properties. All elements other than hydrogen in the first column of the abbreviated table are **alkali metals**—lithium, sodium, and potassium. These are generally soft silvery-white metals of low density that react violently with water to produce hydroxides (LiOH, NaOH, KOH) and with chlorine to produce chlorides (LiCl, NaCl, KCl). The **alkaline earth** metals—beryllium, magnesium, calcium—are in the second column of the table. When freshly cut, these metals have a grayish-white luster. They are chemically reactive and have a strong tendency to form doubly charged cations (Be^{2+}, Mg^{2+}, Ca^{2+}) by losing two electrons from each atom. Another group notable for the very close similarities of the elements in it consists of the **noble gases** in the far right column of the table. Each of these—helium, neon, argon—is a monatomic gas that does not react chemically.

The Elements beyond Calcium

The electron structures of elements beyond atomic number 20 are more complicated than those of the lighter elements. The complete periodic table in Figure 1.3 shows, among the heavier elements, the transition metals, including chromium, manganese, iron, cobalt, nickel, and copper; the lanthanides; and the actinides, including thorium, uranium, and plutonium. The transition metals include a number

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of metals that are important in industry and in life processes. The actinides contain elements familiar to those concerned with nuclear energy, nuclear warfare, and related issues. A list of the known elements through atomic number 109 is given on page 120 at the end of this chapter.

3.11 A MORE DETAILED LOOK AT ATOMIC STRUCTURE

So far, this chapter has covered some important aspects of atoms. These include the facts that an atom is made of three major subatomic particles, and consists of a very small, very dense, positively charged nucleus surrounded by a cloud of negatively charged electrons in constant, rapid motion. The first 20 elements have been discussed in some detail and placed in an abbreviated version of the periodic table. Important concepts introduced so far in this chapter include:

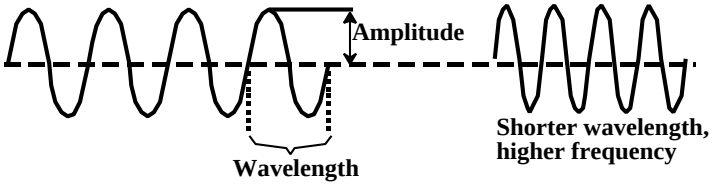
- Dalton's atomic theory
- Electron shells
- Inner shell electrons
- Octet rule
- Lewis symbols to represent outer e^-.
- Significance of filled electron shells
- Outer shell electrons
- Abbreviated periodic table

The information presented about atoms so far in this chapter is adequate to meet the needs of many readers. These readers may choose to forgo the details of atomic structure presented in the rest of this chapter without major harm to their understanding of chemistry. However, for those who wish to go into more detail, or who do not have a choice, the remainder of this chapter discusses in more detail the electronic structures of atoms as related to their chemical behavior and introduces the quantum theory of electrons in atoms.

Electromagnetic Radiation

The **quantum theory** explains the unique behavior of charged particles that are as small and move as rapidly as electrons. Because of its close relationship to electromagnetic radiation, an appreciation of quantum theory requires an understanding of the following important points related to electromagnetic radiation:

- Energy can be carried through space at the speed of light, 3.00×10^9 meters per second (m/s) in a vacuum, by **electromagnetic radiation**, which includes visible light, ultraviolet radiation, infrared radiation, microwaves, and radio waves.
- Electromagnetic radiation has a **wave character**. The waves move at the speed of light, c, and have characteristics of **wavelength** (λ), amplitude, and **frequency** (ν, Greek "nu") as illustrated below:



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- The wavelength is the distance required for one complete cycle and the frequency is the number of cycles per unit time. They are related by the following equation:

$$\nu\lambda = c$$

 where ν is in units of cycles per second (s^{-1}, a unit called the **hertz**, Hz) and λ is in meters (m).

- In addition to behaving as a wave, electromagnetic radiation also has characteristics of particles.
- The dual wave/particle nature of electromagnetic radiation is the basis of the **quantum theory** of electromagnetic radiation, which states that radiant energy can be absorbed or emitted only in discrete packets called **quanta** or **photons**. The energy, E, of each photon is given by

$$E = h\nu$$

 where *h* is Planck's constant, 6.63×10^{-34} J-s (joule x second).
- From the preceding, it is seen that *the energy of a photon is higher when the frequency of the associated wave is higher* (and the wavelength shorter).

3.12 QUANTUM AND WAVE MECHANICAL MODELS OF ELECTRONS IN ATOMS

The *quantum theory* introduced in the preceding section provided the key concepts needed to explain the energies and behavior of electrons in atoms. One of the best clues to this behavior, and one that ties the nature of electrons in atoms to the properties of electromagnetic radiation, is the emission of light by energized atoms. This is easiest to explain for the simplest atom of all, that of hydrogen, which consists of only one electron moving around a nucleus with a single positive charge. Energy added to hydrogen atoms, such as by an electrical discharge through hydrogen gas, is re-emitted in the form of light at very specific wavelengths (656, 486, 434, 410 nm in the visible region). The highly energized atoms that can emit this light are said to be "excited" by the excess energy originally put into them and to be in an **excited state**. The reason for this is that the electrons in the excited atoms are forced farther from the nuclei of the atoms and, when they return to a lower energy state, energy is emitted in the form of light. The fact that very specific wavelengths of light are emitted in this process means that electrons can be present only in specified states at highly specific energy levels. Therefore, the transition from one energy state to a lower one involves the emission of a specific energy of electromagnetic radiation (light). Consider the equation

$$E = h\nu \tag{3.12.1}$$

that relates energy to frequency, ν, of electromagnetic radiation. If a transition of an electron from one excited state to a lower one involves a specific amount of energy,

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E, a corresponding value of ν is observed. This is reflected by a specific wavelength of light according to the following relationship:

$$\lambda = \frac{c}{\nu} \tag{3.12.2}$$

The first accepted explanation of the behavior outlined above was the **Bohr theory** advanced by the Danish physicist Neils Bohr in 1913. Although this theory has been shown to be too simplistic, it had some features that are still pertinent to atomic structure. The Bohr theory visualized an electron orbiting the nucleus (a proton) of the hydrogen atom in orbits. Only specific orbits called **quantum states** were allowed. When energy was added to a hydrogen atom, its electron could jump to a higher orbit. When the atom lost its energy as the electron returned to a lower orbit, the energy lost was emitted in the form of electromagnetic radiation as shown in Figure 3.10. Because the two energy levels are of a definite magnitude according to quantum theory, the energy lost by the electron must also be of a definite energy, $E = h\nu$. Therefore, the electromagnetic radiation (light) emitted is of a specific frequency and wavelength.

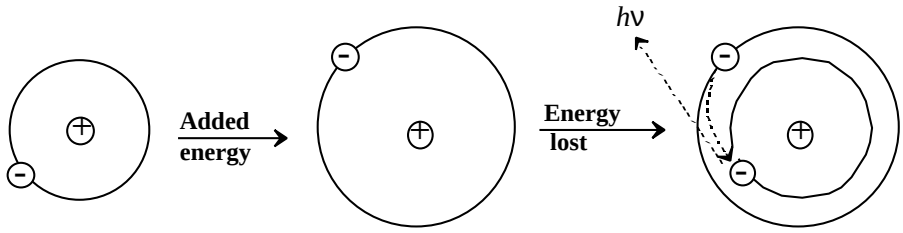


Figure 3.10 According to the Bohr model, adding energy to the hydrogen atom promotes an electron to a higher energy level. When the electron falls back to a lower energy level, excess energy is emitted in the form of electromagnetic radiation of a specific energy, $E = h\nu$.

The Wave Mechanical Model of Atomic Structure

Though shown to have some serious flaws and long since abandoned, the Bohr model laid the groundwork for the more sophisticated theories of atomic structure that are accepted today and introduced the all-important concept that *only specific energy states are allowed for an electron in an atom*. Like electromagetic radiation, electrons in atoms are now visualized as having a dual wave/particle nature. They are treated theoretically by the **wave mechanical model** as **standing waves** around the nucleus of an atom. The idea of a standing wave can be visualized for the string of a musical instrument as represented in Figure 3.11. Such a wave does not move along the length of a string because both ends are anchored, which is why it is called a *standing wave*. Each wave has **nodes**, which are points of zero displacement. Because there must be a node on each end where the string is anchored, the standing waves can only exist as multiples of *half-wavelengths*.

According to the *wave mechanical* or *quantum mechanical* model of electrons in atoms, the known *quantization* of electron energy in atoms occurs because only specific multiples of the standing wave associated with an electron's movement are allowed. Such a phenomenon is treated mathematically with the **Schrödinger equa-**

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tion, resulting from the work of Erwin Schrödinger, first published in 1926. Even for the one-electron hydrogen atom, the mathematics is quite complicated, and no attempt will be made to go into it here. The Schrödinger equation is represented as

$$H\psi = E\psi \qquad (3.12.3)$$

where ψ is the Greek psi. Specifically, ψ is the **wave function**, a function of the electron's energy and the coordinates in space where it may be found. The term H is an **operator** consisting of a set of mathematical instructions, and E is the sum of the kinetic energy due to the motion of the electron and the potential energy of the mutual attraction between the electron and the nucleus.

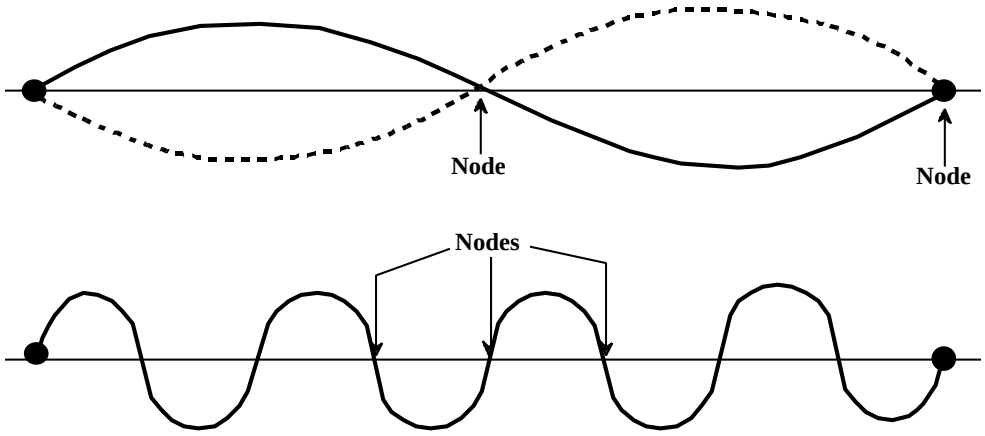


Figure 3.11 A string anchored at both ends (such as on a stringed musical instrument) can only vibrate at multiples of waves or half-waves. The illustration above shows one wave (top) and four waves (bottom). Each point at which a wave intersects the horizontal lines is called a node.

Solutions to the Schrödinger Equation, Electrons in Orbitals

With its movement governed by the laws of quantum mechanics, it is not possible to know where an electron is relative to an atom's nucleus at any specific instant. However, the Schrödinger equation permits calculation of the probability of an electron being in a specified region. Solution of the equation gives numerous wave functions, each of which corresponds to a definite energy level and to the probability of finding an electron at various locations and distances relative to the nucleus (Figure 3.12). The wave function describes **orbitals**, *each of which has a characteristic energy and region around the nucleus where the electron has certain probabilities of being found*. The term orbital is used because quantum mechanical calculations do not give specific orbits consisting of defined paths for electrons, like planets going around the sun.

The square of the wave function, ψ^2, calculated and integrated for a small segment of volume around a nucleus, is proportional to the probability of finding an electron in that small volume, which can be regarded as part of an *electron cloud.* With this view, the electron is more likely to be found in a region where the cloud is relatively more dense. The cloud has no definite outer limits, but fades away with

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increasing distance from the nucleus to regions in which there is essentially no probability of finding the electron.

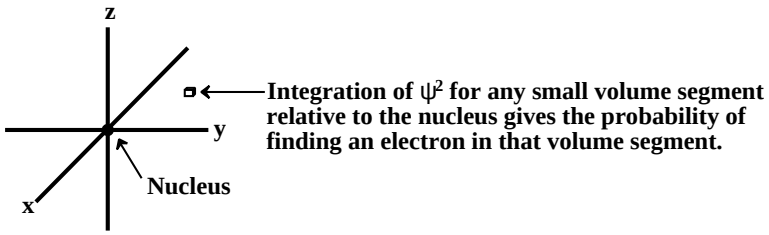


Figure 3.12. The xyz coordinate system used to describe the orientations in space of orbitals around the nucleus of an atom.

Multielectron Atoms and Quantum Numbers

Wave mechanical calculations describe various **energy levels** for electrons in an atom. Each energy level has at least one orbital. *A single orbital may contain a maximum of only two electrons*. Although the Schrödinger approach was originally applied to the simplest atom, hydrogen, it has been extended to atoms with many electrons (multielectron atoms). Electrons in atoms are described by four **quantum numbers**, which are defined and described briefly below. With these quantum numbers and a knowledge of the rules governing their use, it is possible to specify the orbitals allowed in a particular atom. *An electron in an atom has its own unique set of quantum numbers; no two electrons can have exactly identical quantum numbers.*

The Principal Quantum Number, n

Main energy levels corresponding to *electron shells* discussed earlier in this chapter are designated by a **principal quantum number**, **n**. Both the size of orbitals and the magnitude of the average energy of electrons contained therein increase with increasing n. Permitted values of n are 1, 2, 3, . . . , extending through 7 for the known elements.

The Azimuthal Quantum Number, l

Within each main energy level (shell) represented by a principal quantum number, there are **sublevels** (subshells). Each sublevel is denoted by an **azimuthal quantum number**, ***l***. For any shell with a principal quantum number of n, the possible values of *l* are 0, 1, 2, 3, . . . ,(n - 1). This gives the following:

- For n = 1, there is only 1 possible subshell, $l = 0$.
- For n = 2, there are 2 possible subshells, $l = 0, 1$.
- For n = 3, there are 3 possible subshells, $l = 0, 1, 2$.
- For n = 4, there are 4 possible subshells, $l = 0, 1, 2, 3$.

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From the above it is seen that the maximum number of sublevels within a principal energy level designated by n is equal to n. Within a main energy level, sublevels denoted by different values of *l* have slightly different energies. Furthermore, *l* designates *different shapes of orbitals.*

The italicized letters *s, p, d,* and *f,* corresponding to *l* values of 0, 1, 2, and 3, respectively, are frequently used to designate sublevels. The number of electrons present in a given sublevel is limited to 2, 6, 10, and 14 for *s, p, d,* and *f,* sublevels, respectively. It follows that, since each orbital can be occupied by a maximum of 2 electrons, there is only 1 orbital in the *s* sublevel, 3 orbitals in the *p* sublevel, 5 in the *d* and 7 in the *f* . The value of the principal quantum number and the letter designating the azimuthal quantum number are written in sequence to designate both the shell and subshell. For example, 4*d* represents the *d* subshell of the fourth shell.

The Magnetic Quantum Number, m_l

The **magnetic quantum number**, m_l, is also known as the **orientational quantum number**. It designates the orientation of orbitals in space relative to each other and distinguishes orbitals within a subshell from each other. It is called the magnetic quantum number because the presence of a magnetic field can result in the appearance of additional lines among those emitted by electronically excited atoms (that is, in atomic emission spectra). The possible values of m_l in a subshell with azimuthal quantum number *l* are given by $m_l = +l, +(l - 1), \ldots, 0, \ldots, -(l - 1), -l$. As examples, for $l = 0$, the only possible value of m_l is 0, and for $l = 3$, m_l, may have values of 3, 2, 1, 0, -1, -2, -3.

Spin Quantum Number , m_s

The fourth and final quantum number to be considered for electrons in atoms is the **spin quantum number** m_s, which can have values of only $+1/2$ or $-1/2$. It results from the fact that an electron spins in either of two directions and generates a tiny magnetic field with an associated magnetic moment. *Two electrons can occupy the same orbital only if they have opposite spins so that their magnetic moments cancel each other.*

Quantum Numbers Summarized

The information given by each quantum number is summarized below:

- The value of the principal quantum number, n, gives the shell and main energy level of the electron.
- The value of the azimuthal quantum number, *l*, specifies sublevels with somewhat different energies within the main energy levels and describes the shapes of orbitals.
- The magnetic quantum number, m_l, distinguishes the orientations in space of orbitals in a subshell and may provide additional distinctions of orbital shapes.

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- The spin quantum number, m_s, with possible values of only $+1/2$ and $-1/2$, accounts for the fact that each orbital can be occupied by a maximum number of only 2 electrons with opposing spins.

Specification of the values of 4 quantum numbers describes each electron in an atom, as shown in Table 3.3.

Table 3.3 Quantum Numbers for Electrons in Atoms

n[1]	*l*[2]	m_l[3]	m_s[4]	
1	0 (1*s*)	0	($m_s = +1/2$ or $-1/2$)	1 orbital
2	0 (2*s*)	0	($m_s = +1/2$ or $-1/2$)	1 orbital
	1 (2*p*)	-1	($m_s = +1/2$ or $-1/2$)	3 orbitals
		0	($m_s = +1/2$ or $-1/2$)	
		+1	($m_s = +1/2$ or $-1/2$)	
3	0 (3*s*)	0	($m_s = +1/2$ or $-1/2$)	1 orbital
	1 (3*p*)	-1	($m_s = +1/2$ or $-1/2$)	3 orbitals
		0	($m_s = +1/2$ or $-1/2$)	
		+1	($m_s = +1/2$ or $-1/2$)	
	2 (3*d*)	-2	($m_s = +1/2$ or $-1/2$)	5 orbitals
		-1	($m_s = +1/2$ or $-1/2$)	
		0	($m_s = +1/2$ or $-1/2$)	
		+1	($m_s = +1/2$ or $-1/2$)	
		+2	($m_s = +1/2$ or $-1/2$)	
4	0 (4*s*)	0	($m_s = +1/2$ or $-1/2$)	1 orbital
	1 (4*p*)	-1	($m_s = +1/2$ or $-1/2$)	3 orbitals
		0	($m_s = +1/2$ or $-1/2$)	
		+1	($m_s = +1/2$ or $-1/2$)	
	2 (4*d*)	-2	($m_s = +1/2$ or $-1/2$)	5 orbitals
		-1	($m_s = +1/2$ or $-1/2$)	
		0	($m_s = +1/2$ or $-1/2$)	
		+1	($m_s = +1/2$ or $-1/2$)	
		+2	($m_s = +1/2$ or $-1/2$)	
	3 (4*f*)	-3	($m_s = +1/2$ or $-1/2$)	7 orbitals
		-2	($m_s = +1/2$ or $-1/2$)	
		-1	($m_s = +1/2$ or $-1/2$)	
		0	($m_s = +1/2$ or $-1/2$)	
		+1	($m_s = +1/2$ or $-1/2$)	
		+2	($m_s = +1/2$ or $-1/2$)	
		+3	($m_s = +1/2$ or $-1/2$)	

[1] n, principal quantum number denoting an energy level, or shell
[2] *l*, azimuthal quantum number of a sublevel or subshell
[3] m_l, magnetic quantum number designating an orbital; each entry in this column designates an orbital capable of holding 2 electrons with opposing spins.
[4] m_s, spin quantum number, which may have a value of $+1/2$ or $-1/2$.

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For each electron in an atom, the orbital that it occupies and the direction of its spin are specified by values of n, l, m_l, and m_s, assigned to it. These values are unique for each electron; *no two electrons in the same atom can have identical values of all four quantum numbers*. This rule is known as the **Pauli exclusion principle**.

3.13 ENERGY LEVELS OF ATOMIC ORBITALS

Electrons in atoms occupy the lowest energy levels available to them. Figure 3.13 is an energy level diagram that shows the relative energy levels of electrons in various atomic orbitals. Each dash, —, in the figure represents *one* orbital that is a potential slot for *two* electrons with opposing spins.

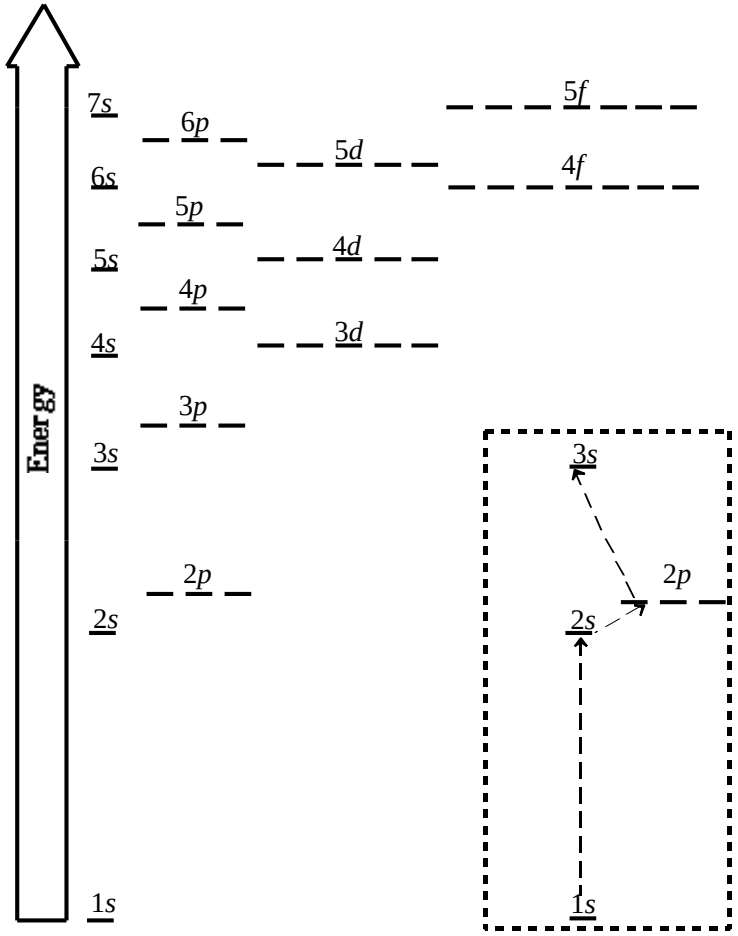


Figure 3.13 Energy levels of atomic orbitals. Each orbital capable of containing 2 electrons is shown with a dash, —. The order of placing electrons in orbitals is from the lowest-lying orbitals up, as shown in the inset.

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The electron energies represented in Figure 3.13 can be visualized as those required to remove an electron from a particular orbital to a location completely away from the atom. As indicated by its lowest postion in the diagram, the most energy would be needed to remove an electron in the 1*s* orbital; comparatively little energy is required to remove electrons from orbitals having higher n values, such as 5, 6, or 7. Furthermore, the diagram shows decreasing separation of the energy levels (values of n) with increasing n. It also shows that some sublevels with a particular value of n have lower energies than sublevels for which the principal quantum number is n - 1. This is first seen from the placement of the 4*s* sublevel below that of the 3*d* sublevel. As a consequence, with increasing atomic number, the 4*s* orbital acquires 2 electrons before any electrons are placed in the 3*d* orbitals.

The value of the principal quantum number, n, of an orbital is a measure of the relative distance of the maximum electron density from the nucleus. An electron with a lower value of n, being on the average closer to the nucleus, is more strongly attracted to the nucleus than an electron with a higher n value that is at a relatively greater distance from the nucleus.

Hund's Rule of Maximum Multiplicity

Orbitals that are in the same sublevel, but that have different values of m_l, have the same energy. This is first seen in the 2*p* sublevel, where the three orbitals with m_l of -1, 0, +1 (shown as three dashes on the same level in Figure 3.13) all have the same energies. The order in which electrons go into such a sublevel follows **Hund's rule of maximum multiplicity**, which states that *electrons in a sublevel are distributed to give the maximum number of unpaired electrons* (that is, those with parallel spins having the same sign of m_s). Therefore, the first three electrons to be placed in the 2*p* sublevel would occupy the three separate available orbitals and would have the same spins. Not until the fourth electron out of a maximum number of 6 is added to this sublevel are two electrons placed in the same orbital.

3.14 SHAPES OF ATOMIC ORBITALS

In trying to represent different shapes of orbitals, it is important to keep in mind that they do not contain electrons within finite volumes, because there is no outer boundary of an orbital at which the probability of finding an electron drops to exactly 0. However, an orbital can be drawn as a figure ("fuzzy cloud") around the atom nucleus within which there is a relatively high probability (typically 90%) of finding an electron within the orbital. These figures are called **contour representations of orbitals** and are as close as one can come to visualizing the shapes of orbitals. Each point on the surface of a contour representation of an orbital has the same value of ψ^2 (square of the wave function of the Schrödinger equation, Section 3.13), and the entire surface encloses the volume within which an electron spends 90% of its time. The two most important aspects of an orbital are its size and shape, both of which are rather well illustrated by a contour representation.

Figure 3.14 shows the contour representations of the first three *s* orbitals. These are spherically shaped and increase markedly in size with increasing principal quantum number, reflecting increased average distance of the electron from the nucleus.

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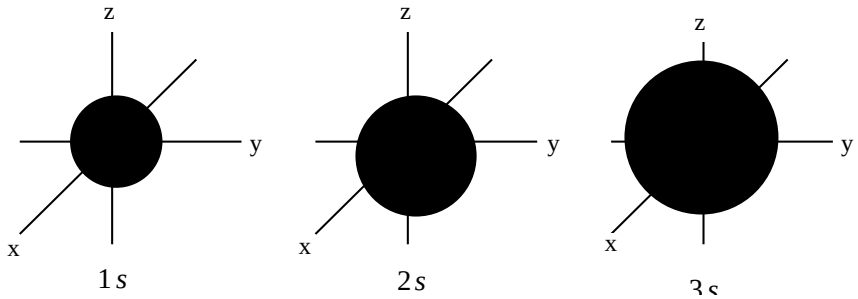


Figure 3.14 Contour representations of s orbitals for the first three main energy levels.

Figure 3.15 shows contour representations of the three 2*p* orbitals. These are seen to have different orientations in space; they have directional properties. In fact, *s* orbitals are the only ones that are spherically symmetrical. The shapes of orbitals are involved in molecular geometry and help to determine the shapes of molecules. The shapes of *d* and *f* orbitals are more complex and variable than those of *p* orbitals and are not discussed in this book.

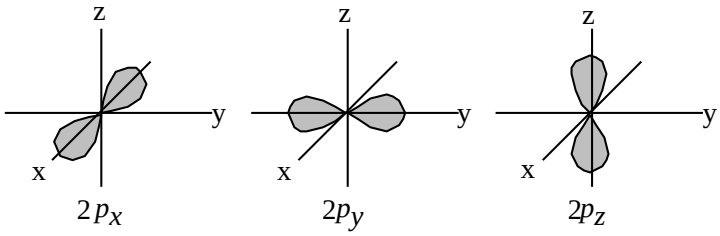


Figure 3.15 Contour representations of 2*p* orbitals.

3.15 ELECTRON CONFIGURATION

Electron configuration is a means of stating which kinds of orbitals contain electrons and the numbers of electrons in each kind of orbital of an atom. It is expressed by the number and letter representing each kind of orbital and superscript numbers telling how many electrons are in each sublevel. The hydrogen atom's one electron in the 1*s* orbital is shown by the following notation:

Sublevel notation

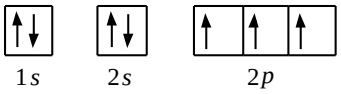
$1s^1$

Number of electrons in sublevel

Nitrogen, atomic number 7, has 7 electrons, of which 2 are paired in the 1*s* orbital, 2 are paired in the 2*s* orbital and 3 occupy singly each of the 3 available 2*p* orbitals. This electron configuration is designated as $1s^2 2s^2 2p^3$.

The **orbital diagram** is an alternative way of expressing electron configurations in which each separate orbital is represented by a box. Individual electrons in the orbitals are shown as arrows pointing up or down to represent opposing spins ($m_s = +1/2$ or $-1/2$). The orbital diagram for nitrogen is the following:

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This gives all the information contained in the notation $1s^2 2s^2 2p^3$, but emphasizes that the three electrons in the three available 2*p* orbitals each occupy separate orbitals, a condition that is a consequence of Hund's rule of maximum multiplicity (Section 3.13).

Most of the remainder of this chapter is devoted to a discussion of the placement of electrons in atoms with increasing atomic number, its effects upon the chemical behavior of atoms, and how it leads to a systematic organization of the elements in the periodic table. This placement of electrons is in the order shown in increasing energy levels from bottom to top in Figure 3.13 as illustrated for nitrogen in Figure 3.16.

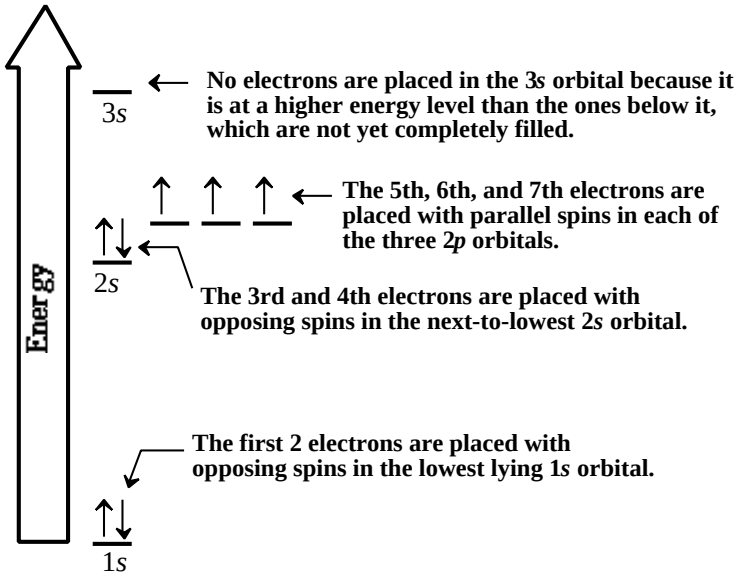


Figure 3.16 Placement of electrons in orbitals for the 7-electron nitrogen atom according to the energy level diagram.

3.16 ELECTRONS IN THE FIRST 20 ELEMENTS

The most meaningful way to place electrons in the orbitals of atoms is on the basis of the periodic table. This enables relating electron configurations to chemical properties and the properties of elements in groups and periods of the periodic table. In this section, electron configurations are deduced for the first 20 elements and given in an abbreviated version of the periodic table.

Electron Configuration of Hydrogen

The 1 electron in the hydrogen atom goes into its lowest-lying 1*s* orbital. Figure 3.17 summarizes all the information available about this electron and its electron configuration.

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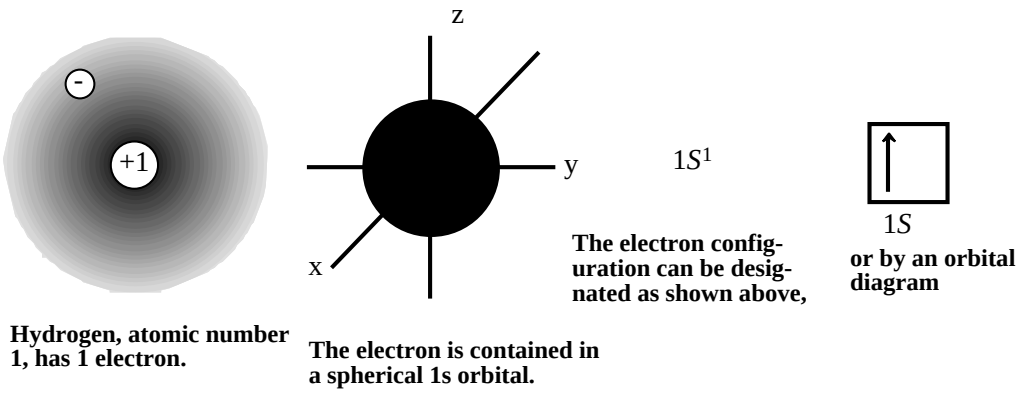


Figure 3.17 Representation of the electron on the hydrogen atom.

Electron Configuration of Helium

An atom of helium, atomic number 2, has 2 electrons, both contained in the 1*s* orbital and having quantum numbers n = 1, $l = 0$, $m_l = 0$, and $m_s = +1/2$ and $-1/2$. Both electrons have the same set of quantum numbers except for m_s. The electron configuration of helium can be represented as $1s^2$, showing that there are 2 electrons in the 1*s* orbital. Two is the maximum number of electrons that can be contained in the first principal energy level; additional electrons in atoms with atomic number greater than 2 must go into principal energy levels with n greater than 1. There are several other noble gas elements in the periodic table, of which neon and argon have already been mentioned, but helium is the only one with a filled shell of 2 electrons—the rest have stable outer shells of 8 electrons.

Electron Configurations of Elements 2–20

The electron configurations of elements with atomic number through 20 are very straightforward. Electrons are placed in order of orbitals with increasing energy as shown in Figure 3.13. This order is

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$

Note that in this configuration the electrons go into the 4*s* orbital before the 3*d* orbital, which lies at a slightly higher energy level. In filling the *p* orbitals, it should also be kept in mind that 1 electron goes into each of three *p* orbitals before pairing occurs. In order to follow the discussion of electron configurations for elements through 20, it is useful to refer to the abbreviated periodic table in Figure 3.20.

Lithium

For lithium, atomic number 3, two electrons are placed in the 1*s* orbital, leaving the third electron for the 2*s* orbital. This gives an electron configuration of $1s^2 2s^1$. The two 1*s* electrons in lithium are in the stable noble gas electron configuration of helium and are very difficult to remove. These are lithium's *inner electrons* and,

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along with the nucleus, constitute the **core** of the lithium atom. The electron configuration *of the core* of the lithium atom is $1s^2$, the same as that of helium. Therefore, the lithium atom is said to have a *helium core*. *The core of any atom consists of its nucleus plus its inner electrons, those with the same electron configuration as the noble gas immediately preceding the element in the periodic table*.

Valence Electrons

Lithium's lone 1*s* electron is an outer electron contained in the *outer shell* of the atom. Outer shell electrons are also called **valence electrons**, and are the electrons that can be shared in covalent bonding or lost to form cations in ionic compounds. Lithium's valence electron is illustrated in Figure 3.18.

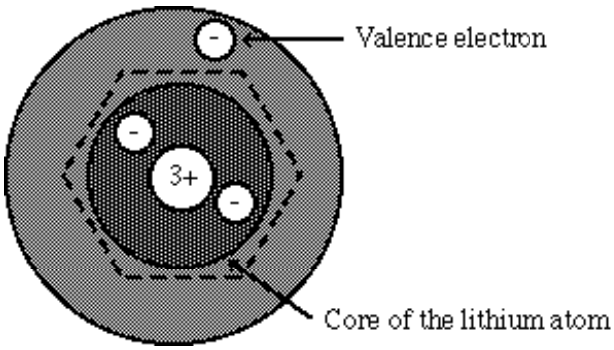


Figure 3.18 Core (kernel) and valence electrons of the lithium atom.

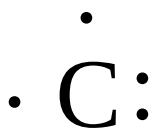
Beryllium

Beryllium, atomic number 4, has 2 inner electrons in the 1*s* orbital and 2 outer electrons in the 2*s* orbital. Therefore, beryllium has a *helium core,* plus 2 *valence electrons*. Its electron configuration is $1s^2 2s^2$.

Filling the 2*p* orbitals

Boron, atomic number 5, is the first element containing an electron in a 2*p* orbital. Its electron configuration is $1s^2 2s^2 2p^1$. Two of the five electrons in the boron atom are contained within the spherical orbital closest to the nucleus, and 2 more are in the larger spherical 2*s* orbital. The lone 2*p* electron is in an approximately dumbell-shaped orbital in which the average distance of the electron from the nucleus is about the same as that of the 2*s* electrons. This electron could have any one of the three orientations in space shown for *p* orbitals in Figure 3.15.

The electron configuration of carbon, atomic number 6, is $1s^2 2s^2 2p^2$. The four outer (valence) electrons are shown by the Lewis symbol



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Two of the four valence electrons are represented by a pair of dots, :, to indicate that these electrons are paired in the same orbital. These are the two 2*s* electrons. The other two are shown as individual dots to represent two unpaired 2*p* electron in separate orbitals.

The 7 electrons in nitrogen, N, are in a $1s^2 2s^2 2p^3$ electron configuration. Nitrogen is the first element to have at least one electron in each of 3 possible *p* orbitals (see Figure 3.19).

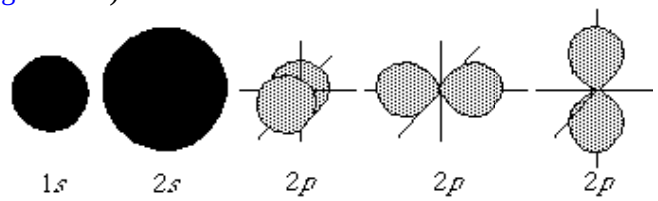
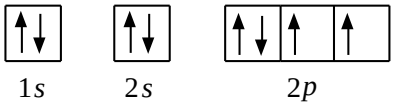
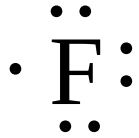


Figure 3.19. The N atom contains 2 electrons in the 1*s* orbital, 2 in the 2*s* orbital, and 1 in each of three separate 2*p* orbitals oriented in different directions in space.

The next element to be considered is oxygen, which has an atomic number of 8. Its electron configuration is $1s^2 2s^2 2p^4$. It is the first element in which it is necessary for 2 electrons to occupy the same *p* orbital, as shown by the following orbital diagrams:



The electron configuration of fluorine, atomic number 9, is $1s^2 2s^2 2p^5$. Its Lewis symbol,



shows that the fluorine atom has only one unpaired electron of the 7 electrons in its valence shell. In its chemical reactions, fluorine seeks to obtain another electron to give a stable *octet*.

Neon, atomic number 10, is at the end of the second period of the periodic table and is a noble gas as shown by its Lewis symbol,



denoting a filled octet of electrons. Its electron configuration is $1s^2 2s^2 2p^6$. In this configuration the $2s^2 2p^6$ portion stands for the outer electrons. Like neon, all other elements with the outer electron configuration $\mathbf{ns^2 np^6}$ are noble gases located in the far right of the periodic table (for example, argon, with the electron configuration $1s^2 2s^2 2p^6 \mathbf{3s^2 3p^6}$).

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Filling the 3*s*, 3*p*, and 4*s* orbitals

The 3*s* and 3*p* orbitals are filled in going across the third period of the periodic table from sodium through argon. Atoms of these elements, like all atoms beyond neon, have their 10 innermost electrons in the neon electron configuration of $1s^2 2s^2 2p^6$. Therefore, these atoms have a *neon core*, which may be designated {Ne}.

{Ne} stands for $1s^2 2s^2 2p^6$

With this notation, the electron configuration of element number 11, sodium may be shown as $\{Ne\}3s^1$, which is an abbreviation for $1s^2 2s^2 2p^6 3s^1$. The former notation has some advantage in simplicity, while showing the outer electrons specifically. In the example just cited it is easy to see that sodium has 1 outer shell 3*s* electron, which it can lose to form the Na^+ ion with its stable noble gas neon electron configuration.

At the end of the third period is located the noble gas argon, atomic number 18, with the electron configuration $1s^2 2s^2 2p^6 3s^2 3p^6$. For elements beyond argon, that portion of the electron configuration identical to argon's may be represented simply as {Ar}. Therefore, the electron configuration of potassium, atomic number 19, is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$, abbreviated $\{Ar\}4\ s^1$, and that of calcium, atomic number 20, is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$, abbreviated $\{Ar\}4\ s^2$. This completes the periodic table through element number 20 as shown in Figure 3.20.

1 H $1s^1$							2 He $1s^2$
3 Li $\{He\}2s^1$	4 Be $\{He\}2s^2$	5 B $\{He\}2s^2 2p^1$	6 C $\{He\}2s^2 2p^2$	7 N $\{He\}2s^2 2p^3$	8 O $\{He\}2s^2 2p^4$	9 F $\{He\}2s^2 2p^5$	10 Ne $\{He\}2s^2 2p^6$
11 Na $\{Ne\}3s^1$	12 Mg $\{Ne\}3s^2$	13 Al $\{Ne\}3s^2 3p^1$	14 Si $\{Ne\}3s^2 3p^2$	15 P $\{Ne\}3s^2 3p^3$	16 S $\{Ne\}3s^2 3p^4$	17 Cl $\{Ne\}3s^2 3p^5$	18 Ar $\{Ne\}3s^2 3p^6$
19 K $\{Ar\}4s^1$	20 Ca $\{Ar\}4s^2$						

Figure 3.20 Abbreviated periodic table showing the electron configurations of the first 20 elements.

3.17 ELECTRON CONFIGURATIONS AND THE PERIODIC TABLE

There are several learning devices to assist expression of the order in which atomic orbitals are filled (electron configuration for each element). However, it is of little significance to express electron configurations without an understanding of the meaning of the configurations. By far the most meaningful way to understand this

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important aspect of chemistry is within the context of the periodic table, as outlined in Figure 3.21. To avoid clutter, only atomic numbers of key elements are shown in this table. The double-pointed arrows drawn horizontally across the periods are labeled with the kind of orbital being filled in that period.

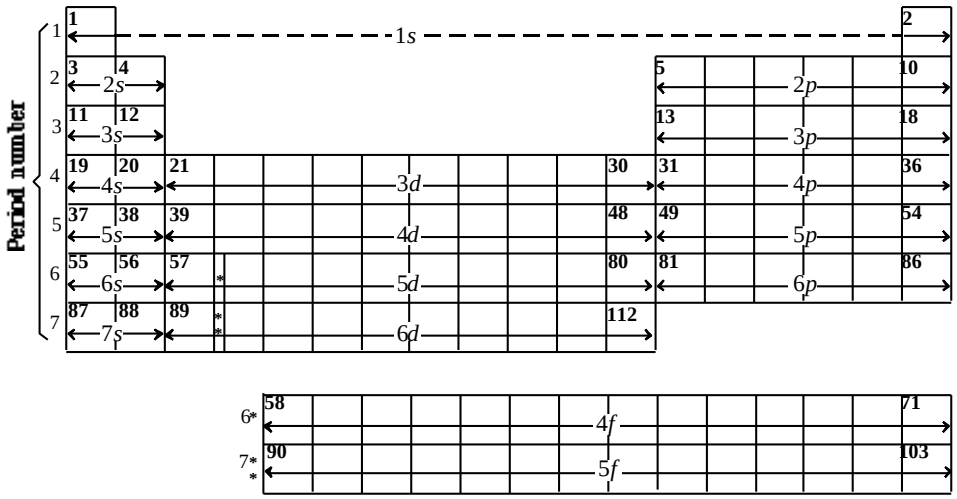


Figure 3.21 Outline of the periodic table labeled to show the filling of atomic orbitals. The type of element being filled with increasing atomic number is shown by the labeled horizontal lines across the periods. The left point of each arrow, ←, marks an element in which the filling of a new kind of orbital starts, and the right point of each arrow, →, marks an element for which the filling of a new kind of orbital is completed. The atomic numbers are given for each element at which the filling of a kind of orbital begins or is completed.

The first step in using the periodic table to figure out electron configurations is to note that the periods are numbered 1 through 7 from top to bottom along the left side of the table. These numbers correspond to the principal quantum numbers (n values) for the orbitals that become filled across the period for both *s* and *p* orbitals. Therefore, in the first group of elements—those with atomic numbers 1, 3, 11, 19, 37, 55, and 87—the last electron added is in the n*s* orbital, for example, 5*s* for Rb, atomic number 37. The last electron added to each of the second group of elements —those with atomic numbers 4, 12, 20, 38, 56, and 88—is the second electron going into the n*s* orbital. For example, in the third period, Mg, atomic number 12, has a filled 3*s* orbital containing 2 electrons. For the group of elements in which the *p* orbitals start to be filled—those in the column with atomic numbers 5, 13, 31, 49, 81—the last electron added to each atom is the first one to enter an n*p* orbital. For example for element 31, Ga, which is contained in the 4th period, the outermost electron is in the 4*s* orbital. In going to the right across each period in this part of the periodic table, the outermost electrons are, successively, np^2, np^3, np^4, np^5, and np^6. Therefore, for elements with atomic numbers 14, 15, 16, 17, and 18 in the 3rd period, the outermost electrons are 3p^2, 3p^3, 3p^4, 3p^5, and 3p^6. Each of the noble gases beyond helium has filled n*p* orbitals with a total of 6 outermost *p* electrons in the three n*p* orbitals.

Each set of five *d* orbitals becomes filled for the *transition metals* in the three horizontal periods beginning with atomic numbers 21, 39, and 57 and ending with, successively, atomic numbers 30, 48, and 80. *For each of these orbitals the value of*

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*n is **1 less** than the period number in which the orbitals become filled*. The first *d* orbitals to become filled are the lowest-lying ones possible, the 3*d* orbitals, which become filled in the fourth period. Across the 5th period, where the 5*s* and 5*p* orbitals become filled for elements 37-38 and 49-54, respectively, the 4*d* orbitals (n 1 less than the period number) become filled for the transition metals, atomic numbers 39-48.

Below the main body of the periodic table are the **inner transition elements** consisting of two rows of elements that are actually parts of the 6th and 7th periods, respectively. The first *f* orbitals begin to fill with the first of the *lanthanides*, element number 58 (Figure 3.26). The principal quantum numbers of their *f* orbitals are *2 less than* their period numbers. These are 4*f* orbitals, of which there are 7 that are filled completely with element number 71. The 4*f* orbitals are filled in the *6th* period. The 5*f* orbitals are filled with the actinide elements, atomic numbers 90-103.

With Figure 3.26 in mind, it is possible to write the expected electron configurations of any of the elements; these are given for all elements in Table 3.4. Consider the following examples:

- Atomic No. 16, S: 3rd period, 16 electrons, Ne core, outermost electrons 3*p*, electron configuration {Ne}$3s^2 3p^4$
- Atomic No. 23, V: 4th period, 23 electrons, Ar core, outermost electrons 3*d*, electron configuration {Ar}$4s^2 3d^3$
- Atomic No. 35, Br: 4th period, 35 electrons, Ar core, all 3*d* orbitals filled, outermost electrons 4*p*, electron configuration {Ne}$4s^2 3d^{10} 4p^5$
- Atomic No. 38, Sr: 5th period, 38 electrons, Kr core, outermost electrons 5*s*, electron configuration {Kr}$5s^2$
- Atomic No. 46, Pd: 5th period, 46 electrons, Kr core, outermost electrons 4*d*, electron configuration {Kr}$5s^2 4d^8$
- Atomic No. 77, Ir: 6th period, 77 electrons, Xe core, all 4*f* orbitals filled in the 6th period, outermost electrons 5*d*, electron configuration {Xe}$6s^2 4f^{14} 5d^7$

Considering the above, it is possible to write the expected electron configurations of any of the elements. The actual electron configurations are given in Table 3.4. In some cases, these vary slightly from those calculated according to the rules. outlined above. These exceptions occur because of the relatively higher stabilities of two half-filled sets of outermost orbitals, or orbitals in which one is half-filled and one entirely filled. The examples below illustrate this point:

- Cr, atomic number 24. Rules predict {Ar}$4s^2 3d^4$. However the actual electron configuration is {Ar}$4s^1 3d^5$ because this gives the slightly more stable electron configuration with *half-filled* 4*s and* 3*d* orbitals.
- Cu, atomic number 29. Rules predict {Ar}$4s^2 3d^9$. However the actual electron configuration is {Ar}$4s^1 3d^{10}$ because this gives *half-filled* 4*s* and *filled* 3*d* orbitals.

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Table 3.4 Electron Configurations of the Elements

Atomic number	Symbol	Electron configuration	Atomic number	Symbol	Electron configuration
1	H	$1s^1$	55	Cs	{Xe}$6s^1$
2	He	$1s^2$	56	Ba	{Xe}$6s^2$
3	Li	{He}$2s^1$	57	La	{Xe}$6s^25d^1$
4	Be	{He}$2s^2$	58	Ce	{Xe}$6s^24f^15d^1$
5	B	{He}$2s^22p^1$	59	Pr	{Xe}$6s^24f^3$
6	C	{He}$2s^22p^2$	60	Nd	{Xe}$6s^24f^4$
7	N	{He}$2s^22p^3$	61	Pm	{Xe}$6s^24f^5$
8	O	{He}$2s^22p^4$	62	Sm	{Xe}$6s^24f^6$
9	F	{He}$2s^22p^5$	63	Eu	{Xe}$6s^24f^7$
10	Ne	{He}$2s^22p^6$	64	Gd	{Xe}$6s^24f^75d^1$
11	Na	{Ne}$3s^1$	65	Tb	{Xe}$6s^24f^9$
12	Mg	{Ne}$3s^2$	66	Dy	{Xe}$6s^24f^{10}$
13	Al	{Ne}$3s^23p^1$	67	Ho	{Xe}$6s^24f^{11}$
14	Si	{Ne}$3s^23p^2$	68	Er	{Xe}$6s^24f^{12}$
15	P	{Ne}$3s^23p^3$	69	Tm	{Xe}$6s^24f^{13}$
16	S	{Ne}$3s^23p^4$	70	Yb	{Xe}$6s^24f^{14}$
17	Cl	{Ne}$3s^23p^5$	71	Lu	{Xe}$6s^24f^{14}5d^1$
18	Ar	{Ne}$3s^23p^6$	72	Hf	{Xe}$6s^24f^{14}5d^2$
19	K	{Ar}$4s^1$	73	Ta	{Xe}$6s^24f^{14}5d^3$
20	Ca	{Ar}$4s^2$	74	W	{Xe}$6s^24f^{14}5d^4$
21	Sc	{Ar}$4s^23d^1$	75	Re	{Xe}$6s^24f^{14}5d^5$
22	Ti	{Ar}$4s^23d^2$	76	Os	{Xe}$6s^24f^{14}5d^6$
23	V	{Ar}$4s^23d^3$	77	Ir	{Xe}$6s^24f^{14}5d^7$
24	Cr	{Ar}$4s^13d^5$	78	Pt	{Xe}$6s^14f^{14}5d^9$
25	Mn	{Ar}$4s^23d^5$	79	Au	{Xe}$6s^14f^{14}5d^{10}$
26	Fe	{Ar}$4s^23d^6$	80	Hg	{Xe}$6s^24f^{14}5d^{10}$
27	Co	{Ar}$4s^23d^7$	81	Tl	{Xe}$6s^24f^{14}5d^{10}6p^1$
28	Ni	{Ar}$4s^23d^8$	82	Pb	{Xe}$6s^24f^{14}5d^{10}6p^2$
29	Cu	{Ar}$4s^13d^{10}$	83	Bi	{Xe}$6s^24f^{14}5d^{10}6p^3$
30	Zn	{Ar}$4s^23d^{10}$	84	Po	{Xe}$6s^24f^{14}5d^{10}6p^4$
31	Ga	{Ar}$4s^23d^{10}4p^1$	85	At	{Xe}$6s^24f^{14}5d^{10}6p^5$
32	Ge	{Ar}$4s^23d^{10}4p^2$	86	Rn	{Xe}$6s^24f^{14}5d^{10}6p^6$
33	As	{Ar}$4s^23d^{10}4p^3$	87	Fr	{Rn}$7s^1$
34	Se	{Ar}$4s^23d^{10}4p^4$	88	Ra	{Rn}$7s^2$
35	Br	{Ar}$4s^23d^{10}4p^5$	89	Ac	{Rn}$7s^26d^1$
36	Kr	{Ar}$4s^23d^{10}4p^6$	90	Th	{Rn}$7s^26d^2$
37	Rb	{Kr}$5s^1$	91	Pa	{Rn}$7s^25p^26d^1$
38	Sr	{Kr}$5s^2$	92	U	{Rn}$7s^25p^36d^1$
39	Y	{Kr}$5s^24d^1$	93	Np	{Rn}$7s^25f^46d^1$
40	Zr	{Kr}$5s^24d^2$	94	Pu	{Rn}$7s^25f^6$
41	Nb	{Kr}$5s^14d^4$	95	Am	{Rn}$7s^25f^7$
42	Mo	{Kr}$5s^14d^5$	96	Cm	{Rn}$7s^25f^76d^1$
43	Tc	{Kr}$5s^24d^5$	97	Bk	{Rn}$7s^25f^9$
44	Ru	{Kr}$5s^14d^7$	98	Cf	{Rn}$7s^25f^{10}$
45	Rh	{Kr}$5s^14d^8$	99	Es	{Rn}$7s^25f^{11}$
46	Pd	{Kr}$4d^{10}$	100	Fm	{Rn}$7s^25f^{12}$
47	Ag	{Kr}$5s^14d^{10}$	101	Md	{Rn}$7s^25f^{13}$
48	Cd	{Kr}$5s^24d^{10}$	102	No	{Rn}$7s^25f^{14}$
49	In	{Kr}$5s^24d^{10}5p^1$	103	Lr	{Rn}$7s^25f^{14}6d^1$
50	Sn	{Kr}$5s^24d^{10}5p^2$	104	Rf	{Rn}$7s^25f^{14}6d^2$
51	Sb	{Kr}$5s24d^{10}5p^3$	105	Ha	{Rn}$7s^25f^{14}6d^3$
52	Te	{Kr}$5s24d^{10}5p^4$	106	Unh	{Rn}$7s^25f^{14}6d^4$
53	I	{Kr}$5s24d^{10}5p^5$	107	Uns	{Rn}$7s^25f^{14}6d^5$
54	Xe	{Kr}$5s24d^{10}5p^6$	108	---	{Rn}$7s^25f^{14}6d^6$
			109	Une	{Rn}$7s^25f^{14}6d^7$

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CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Briefly, the basic parts of the atomic theory are [1]_____ _____, [2]_____ _____, [3]_____ _____, [4]_____ _____, and [5]_____. Three fundamental laws that are explained by the atomic theory are [6]_____ _____, [7]_____, and [8]_____ _____The atomic mass unit is used to [9]_____ _____ and is defined as [10]_____ _____. Most of the volume of an atom is composed of [11]_____. The three subatomic particles of concern to chemists, their charges, and mass numbers are[12]_____ _____. The atomic number and mass number of $^{14}_{7}N$ are [13]_____. A systematic arrangement of elements that places those with similar chemical properties and electron configurations in the same groups is the [14] _____ _____. Most hydrogen atoms have a nucleus consisting of [15]_____. The notation Ca: is an example of [16]_____ and H:H is an example of [17]_____. Helium is the first element with a [18]_____. Lithim is the first element having both [19]_____ and [20]_____ electrons. Four general characteristics of metals are [21]_____ _____. The Lewis symbols of elements 3–10 are [22]_____ _____.The octet rule is [23]_____ _____. The names of the elements in the third period of the periodic table are [24]_____ _____. The noble gases in the first 20 elements are [25]_____. The unique behavior of charged particles that are as small and move as rapidly as electrons is explained by [26]_____. Electromagnetic radiation has a characteristic [27]_____and [28]_____ related by the equation [29]_____. According to the quantum theory, radiant energy may be absorbed or emitted only in discrete packets called [30]_____ _____, the energy of which is given by the equation [31]_____. The Bohr model introduced the all-important concept that [32]_____ _____.

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The wave mechanical model of electrons treats them as [33]_____ _____ around the nucleus of an atom. The wave mechanical model of electrons in atoms is treated by the [34]_____ equation expressed mathematically as [35]_____. In this equation ψ is the [36]_____ and is a function of the electron's [37]_____ _____. According to the wave mechanical model electrons occupy [38]_____ each of which has [39]_____ _____. A single orbital can contain a maximum of [40]___ electrons. An electron in an atom is described by four [41]_____ which may not be [42]_____ for any two electrons in an atom. The symbol n represents the [43]_____ which may have values of [44]_____. The symbol *l* represents the [45]_____ quantum number, which can have values of [46]_____ _____. The symbol m_l represents [47]_____ with possible values of [48]_____. The symbol m_s is the [49]_____ which may have values of only [50]_____. Using standard notation for electron configuration (starting $1s^2 2s^2 2p^6$) the order of filling of orbitals and the maximum number of electrons in each is [51]_____. The orbital diagram for the *p* electrons in nitrogen,



illustrates the rule that [52]_____ _____. The entire surface of a contour representation of an orbital encloses [53]_____ _____. The contour representation of an *s* orbital is that of [54]_____ whereas that of a *p* orbital is shaped like a [55]_____. [56]_____ is a means of stating which kinds of orbitals contain electrons and the numbers of electrons in each kind of orbital of an atom. It is expressed by the number and letter representing [57]_____ and superscript numbers telling [58]_____. The electron configurations of phosphorus (P), potassium (K), and arsenic (As) are, respectively, [59]_____. The part of an atom consisting of its nucleus and the electrons in it equivalent to those of the noble gas immediately preceding the element in the periodic table is the [60]_____ of the atom. The electronic configuration *of the core* of the lithium atom is $1s^2$, the same as that of helium. Therefore, the lithium atom is said to have a [61]_____. Electrons that can be shared in covalent bonding or lost to form cations in ionic compounds are called [62]_____. All elements with the outer electron configuration ns^2np^6 are [63]_____. In respect to period number in the periodic table, the principal quantum number of *s* electrons is [64]_____, that of *p* electrons is [65]_____ _____, that of *d* electrons is [66]_____ _____, and that of *f* electrons is [67]_____ _____. The types of elements in which *d* orbitals become filled are [68]_____ _____. The electron configuration of Cr, atomic number 24, is $\{Ar\}4s^1 3d^5$,

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which appears to deviate slightly from the rules because it gives a [69]_____ _____.

Answers to Chapter Summary

1. Elements are composed of small objects call atoms.
2. Atoms of different elements do not have identical chemical properties.
3. Chemical compounds are formed by combination of atoms of different elements in definite ratios.
4. Chemical reactions involve the separation and combination of atoms.
5. During the course of ordinary chemical reactions, atoms are not created, destroyed, or changed to atoms of other elements.
6. law of conservation of mass
7. law of multiple proportions
8. law of constant composition
9. express masses of atoms
10. exactly 1/12 mass of carbon-12 isotope
11. electrons around the nucleus
12. proton (+1, 1), electron (-1, 0), neutron (0, 1)
13. 7 and 14
14. periodic table
15. 1 proton
16. an electron-dot symbol or Lewis symbol
17. an electron-dot formula or Lewis formula
18. filled electron shell
19. inner
20. outer
21. luster, malleable, conduct electricity, tend to lose electrons to form cations
22. 3 Li·, 4 Be:, 5 ·B:, 6 ·C:, 7 ·N:, 8 ·O:, 9 ·F:, 10 :Ne:
23. the tendency of elements to acquire an 8-electron outer electron configuration in chemical compounds
24. sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, and argon
25. helium, neon, argon
26. quantum theory
27. wavelength
28. frequency
29. $\nu\lambda = c$
30. quanta or photons
31. $E = h\nu$
32. only specific energy states are allowed for an electron in an atom
33. standing waves
34. Schrödinger equation
35. $H\psi = E\psi$
36. wave function
37. energy and the coordinates in space where it may be found
38. orbitals

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39. characteristic energy and region around the nucleus where the electron has certain probabilities of being found
40. two
41. quantum numbers
42. identical
43. principal
44. 1, 2, 3, 4, 5, 6, 7. . .
45. azimuthal
46. 0, 1, 2, 3, . . . ,(n - 1)
47. magnetic quantum number
48. $+l$, $+(l - 1)$, . . . ,0, . . . , $-(l - 1)$, $-l$
49. spin quantum number
50. $+1/2$ or $-1/2$
51. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2$
52. electrons in a sublevel are distributed to give the maximum number of unpaired electrons
53. the volume within which an electron spends 90% of its time
54. a sphere
55. dumbell, or two "pointed" spheres touching at the nucleus
56. Electron configuration
57. each kind of orbital
58. how many electrons are in each sublevel
59. $1s^2 2s^2 2p^6 3s^2 3p^3$, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$, $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$
60. core
61. helium core
62. valence electrons
63. noble gases located in the far right of the periodic table
64. the same as the period number
65. the same as the period number
66. one less than the period number
67. two less than the period number
68. transition metals
69. slightly more-stable electron configuration with half-filled 4*s* and 3*d* orbitals

QUESTIONS AND PROBLEMS

Section 3.2. The Atomic Theory

1. Match the law or observation denoted by letters below with the portion of Dalton's atomic theory that explains it denoted by numbers:

 A. Law of Conservation of Mass
 B. Law of Constant Composition
 C. Law of Multiple Proportions
 D. The reaction of C with O_2 does not produce SO_2.

 1. Chemical compounds are formed by the combination of atoms of different elements in definite constant ratios that usually can be expressed as integers or simple fractions.

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2. During the course of ordinary chemical reactions, atoms are not created or destroyed
3. During the course of ordinary chemical reactions, atoms are not changed to atoms of other elements.
4. Illustrated by groups of compounds such as $CHCl_3$, CH_2Cl_2, or CH_3Cl.

2. Particles of pollutant fly ash may be very small. Estimate the number of atoms in such a small particle assumed to have the shape of a cube that is 1 micrometer (μm) to the side. Assume also that an atom is shaped like a cube 100 picometers (pm) on a side.
3. Explain why it is incorrect to say that atomic mass is the mass of any atom of an element. How is atomic mass defined?

Section 3.3. Subatomic Particles

4. The $^{12}_{6}C$ isotope has a mass of exactly 12 u. Compare this with the sum of the masses of the subatomic particles that compose this isotope. Is it correct to say that the mass of an isotope is exactly equal to the sum of the masses of its subatomic particles? Is it close to the sum?
5. What is the distinction between the mass of a subatomic particle and its mass number?
6. Add up the masses of all the subatomic particles in an isotope of carbon-12. Is the sum exactly 12? Should it be?
7. Fill in the blanks in the table below

Subatomic particle	Symbol	Unit Charge	Mass number	Mass in u	Mass in grams
Proton	(a)_____	(b)_____	(c)_____	(d)_____	(e)_____
(f)_____	*n*	0	1	(g)_____	(h)_____
Electron	*e*	(i)_____	(j)_____	(k)_____	9.1096×10^{-28}

Section 3.4. The Basic Structure of the Atom

8. Define what is meant by *x*, *y*, and A in the notation $^{y}_{x}A$.
9. Describe what happens to the magnitude and direction of the forces between charged particles (electrons, protons, nuclei) of (a) like-charge and (b) unlike charge with distance and magnitude of charge.

Section 3.6. Hydrogen, the Simplest Atom

10. What is the Lewis symbol of hydrogen and what does it show? What is the Lewis formula of H_2 and what does it show?
11. In many respects the properties of elemental hydrogen are unique. List some of these properties and some of the major uses of H_2.

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Section 3.7. Helium, the First Atom with a Filled Electron Shell

12. Give the Lewis symbol of helium and explain what it has to do with (a) electron shell, (b) filled electron shell, (c) and noble gases.
13. Where is helium found, and for what purpose is it used?

Section 3.8. Lithium, The First Atom with Both Inner and Outer Electrons

14. Using dots to show <u>all</u> of its electrons, give the Lewis symbol of Li. Explain how this symbol shows (a) inner and outer electrons and electron shells, (b) valence electrons, (c) and how Li^+ ion is formed.
15. Discuss the chemical and physical properties of lithium that indicate that it is a metal.

Section 3.9. The Second Period, Elements 4-10

16. What is a particular health concern with beryllium?
17. Based upon its electronic structure, suggest why boron behaves like a metalloid, showing properties of both metals and nonmetals.
18. Carbon has two isotopes that are of particular importance. What are they and why are they important?
19. Why might carbon be classified as a "life element"?
20. What two species other than O_2 are possible for elemental oxygen, particularly in the stratosphere:
21. What do particular kinds of fluorine compounds have to do with atmospheric ozone?
22. In reference to neon define and explain the significance of (a) noble gas, (b) octet of outer shell electrons, (c) noble gas outer electron configuration, (d) octet rule.

Section 3.10. Elements 11-20, and Beyond

23. To which class of elements do lithium, sodium, and potassium belong? What are their elemental properties?

Section 3.11. A More Detailed Look at Atomic Structure

24. Define and explain (a) electromagnetic radiation, (b) wave character of electromagnetic radiation, (c) quanta (photons).

Section 3.12. Quantum and Wave Mechanical Models of Electrons in Atoms

25. What is the significance of the fact that very specific wavelengths of light are emitted when atoms in an excited state revert back to a lower energy state (ground state)?

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26. What are the major accomplishments and shortcomings of the Bohr theory?

27. How are electrons visualized in the wave mechanical model of the atom?

28. What is the fundamental equation for the the wave mechanical or quantum mechanical model of electrons in atoms? What is the significance of ψ in this equation?

29. Why are orbitals not simply called "orbits" in the quantum mechanical model of atoms?

30. Name and define the four quantum numbers used to describe electrons in atoms.

31. What does the Pauli exclusion principle say about electrons in atoms?

Section 3.13. Energy Levels of Atomic Orbitals

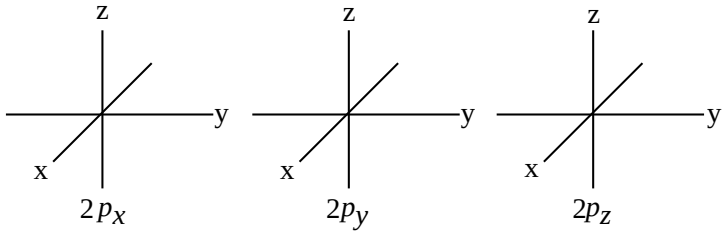
32. Use the notation employed for electron configurations to denote the order in which electrons are placed in orbitals through the 4*f* orbitals.

33. What is a statement and significance of Hund's Rule of Maximum Multiplicity?

Section 3.14. Shapes of Atomic Orbitals

34. Discuss shapes and sizes of *s* orbitals with increasing principal quantum number.

35. Complete the figure below for contour representations of the three 2*p* orbitals.



3.15. Electron Configuration

36. An atom of nitrogen has an electron configuration of $1s^2 2s^2 2p^3$. Give the electron con-figuration of an atom with 5 more electrons and also give the orbital diagram of such an atom.

3.16. Electrons in the First 20 Elements

37. Give the electron configurations of carbon, neon, aluminum, phosphorus and calcium.

38. Give the symbols of the elements with the following electron configurations:

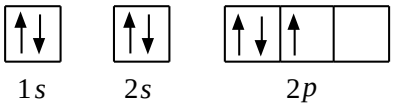
 (a) $1s^2 2s^3$
 (b) $1s^2 2s^2 2p^6 3s^1$
 (c) $1s^2 2s^2 2p^6 3s^2 3p^4$
 (d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$.

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39. What is the core of an atom? Specifically, what is the neon core?

40. What are valence electrons? What are the electron configurations of the valence electrons in aluminum?

41. What is wrong with the orbital diagram below?



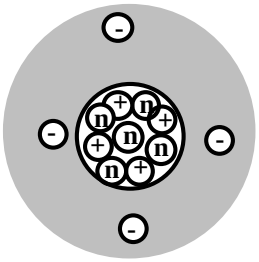
Section 3.17. Electron Configurations and the Periodic Table

42. State the rule that gives which orbitals are filled for transition elements in relation to the period number of the elements involved. Do the same for the inner transition elements.

43. Explain why the electron configuration of Cr is $\{Ar\}4s^1 3d^5$ and why that of Cu, is $\{Ar\}4s^1 3d^{10}$.

General Questions

44. The isotope,



could be designated as

A $^{7}_{3}Li$, B. $^{9}_{4}Be$, C. $^{11}_{5}B$, D. $^{13}_{6}C$, E. $^{20}_{10}Ne$

45. Of the following, the statement that is part of Dalton's atomic theory is

A. Atoms of different elements are likely to have identical chemical properties.

B. Two or more different elements combine in definite, constant ratios to form chemical compounds.

C. Atoms of one element may be converted to atoms of other elements during chemical reactions.

D. The total mass of the products of chemical reactions may be different from the total mass of the reactants.

E. Each element is composed of diatomic molecules, such as O_2.

46. Four of the following elements share a common characteristic insofar as they related to the periodic table. The one that does not share this characteristic is

A. Neon B. Carbon C. Calcium D. Oxygen E. Nitrogen

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47. Of the following, the statement that is **untrue** pertaining to atoms is

A. About half of the volume is contained in the nucleus.
B. Essentially all of the mass is in the nucleus.
C. Essentially all the volume is composed of a cloud of electrons.
D. An atom of ${}^{1}_{1}H$ has no neutrons.
E. A neutral atom has equal numbers of protons and electrons.

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List of the Elements[1]

Atomic number	Name	Symbol	Atomic mass	Atomic number	Name	Symbol	Atomic mass
1	Hydrogen	H	1.00794	56	Barium	Ba	137.327
2	Helium	He	4.0026	57	Lanthanum	La	138.9055
3	Lithium	Li	6.941	58	Cerium	Ce	140.115
4	Beryllium	Be	9.01218	59	Praseodymium	Pr	140.9077
5	Boron	B	10.811	60	Neodymium	Nd	144.24
6	Carbon	C	12.011	61	Promethium	Pm	145
7	Nitrogen	N	14.0067	62	Samarium	Sm	150.36
8	Oxygen	O	15.9994	63	Europium	Eu	151.965
9	Fluorine	F	18.9984	64	Gadolinium	Gd	157.25
10	Neon	Ne	20.1797	65	Terbium	Tb	158.925
11	Sodium	Na	22.9898	66	Dysprosium	Dy	162.50
12	Magnesium	Mg	24.305	67	Holmium	Ho	164.9303
13	Aluminum	Al	26.98154	68	Erbium	Er	167.26
14	Silicon	Si	28.0855	69	Thulium	Tm	168.9342
15	Phosphorus	P	30.9738	70	Ytterbium	Yb	173.04
16	Sulfur	S	32.066	71	Lutetium	Lu	174.967
17	Chlorine	Cl	35.4527	72	Hafnium	Hf	178.49
18	Argon	Ar	39.948	73	Tantalum	Ta	180.9497
19	Potassium	K	39.0983	74	Tungsten	W	183.85
20	Calcium	Ca	40.078	75	Rhenium	Re	186.207
21	Scandium	Sc	44.9559	76	Osmium	Os	190.2
22	Titanium	Ti	47.88	77	Iridium	Ir	192.22
23	Vanadium	V	50.9415	78	Platinum	Pt	195.08
24	Chromium	Cr	51.9961	79	Gold	Au	196.9665
25	Manganese	Mn	54.938	80	Mercury	Hg	200.59
26	Iron	Fe	55.847	81	Thallium	Tl	204.383
27	Cobalt	Co	58.9332	82	Lead	Pb	207.2
28	Nickel	Ni	58.6934	83	Bismuth	Bi	208.98
29	Copper	Cu	63.546	84	Polonium	Po	209
30	Zinc	Zn	65.39	85	Astatine	At	210
31	Gallium	Ga	69.723	86	Radon	Rn	222
32	Germanium	Ge	72.61	87	Francium	Fr	223
33	Arsenic	As	74.9216	88	Radium	Ra	226.0254
34	Selenium	Se	78.96	89	Actinium	Ac	227.0278
35	Bromine	Br	79.904	90	Thorium	Th	232.038
36	Krypton	Kr	83.8	91	Protactinium	Pa	231.0359
37	Rubidium	Rb	85.4678	92	Uranium	U	238.0289
38	Strontium	Sr	87.62	93	Neptunium	Np	237.048
39	Yttrum	Y	88.9056	94	Plutonium	Pu	244
40	Zirconium	Zr	91.224	95	Americium	Am	243
41	Niobium	Nb	92.9064	96	Curium	Cm	247
42	Molybdenum	Mo	95.94	97	Berkelium	Bk	247
43	Technetium	Tc	98	98	Californium	Cf	251
44	Ruthenium	Ru	101.07	99	Einsteinium	Es	252
45	Rhodium	Rh	102.9055	100	Fermium	Fm	257.1
46	Palladium	Pd	106.42	101	Mendelevium	Md	258.1
47	Silver	Ag	107.8682	102	Nobelium	No	255
48	Cadmium	Cd	112.411	103	Lawrencium	Lr	260
49	Indium	In	114.82	104	Ruthefordium	Rf	261.11
50	Tin	Sn	118.710	105	Dubnium	Db	262.11
51	Antimony	Sb	121.757	106	Seaborgium	Sg	263.12
52	Tellurium	Te	127.60	107	Bohrium	Bh	262.12
53	Iodine	I	126.9045	108	Hassium	Hs	265
54	Xenon	Xe	131.29	109	Meitnerium	Mt	266
55	Cesium	Cs	132.9054				

[1] Elements above atomic number 92 have been made artificially.

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Fundamentals of Environmental Chemistry
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4 CHEMICAL BONDS, MOLECULES, AND COMPOUNDS

4.1 CHEMICAL BONDS AND COMPOUND FORMATION

Chemical compounds and chemical bonds have already been mentioned several times in this book. It is not possible to even begin the study of chemistry without some knowledge of compounds and bonding because they are the essence of chemical science. The first three chapters of this book have provided an overview of chemistry, a discussion of the properties of matter, and an explanation of atoms, and elements. With this background it is possible to discuss chemical bonds, molecules, and compounds in more detail.

By now the reader should have an appreciation of the diversity of types of chemical compounds, all formed from just a few elements. This variety is possible because atoms of the elements are joined together through chemical bonds. The chemical behavior of the elements can only be understood with a knowledge of their abilities to form chemical bonds. Shapes and structures of molecules are determined by the orientation of chemical bonds attached to the atoms composing the elements. The strengths of chemical bonds in a compound largely determine its stability and resistance to chemical change. For example, photons (as represented by the symbol $h\nu$, see Section 3.11) of sunlight in the ultraviolet and shorter wavelength regions of the visible light spectrum can be absorbed by a molecule of nitrogen dioxide, NO_2, and break a chemical bond between an N and O atom,

$$NO_2 \xrightarrow{h\nu} NO + O \qquad (4.1.1)$$

yielding very reactive atoms of oxygen. These atoms attack hydrocarbons (compounds composed of C and H) introduced as pollutants into the atmosphere from incompletely burned automobile exhaust gases and other sources. This sets off a series of reactions—chain reactions—that lead to the production of atmospheric ozone, formaldehyde, additional NO_2, and other products known as photochemical smog (see Figure 4.1).

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Chemical Bonds and Valence Electrons

Chemical bonds are normally formed by the transfer or sharing of *valence electrons*, those that are in the *outermost shell* of the atom (see Section 3.8). To visualize how this is done, it is helpful to consider the first 20 elements in the periodic table and their valence electrons represented by Lewis symbols, as shown in Figure 4.2.

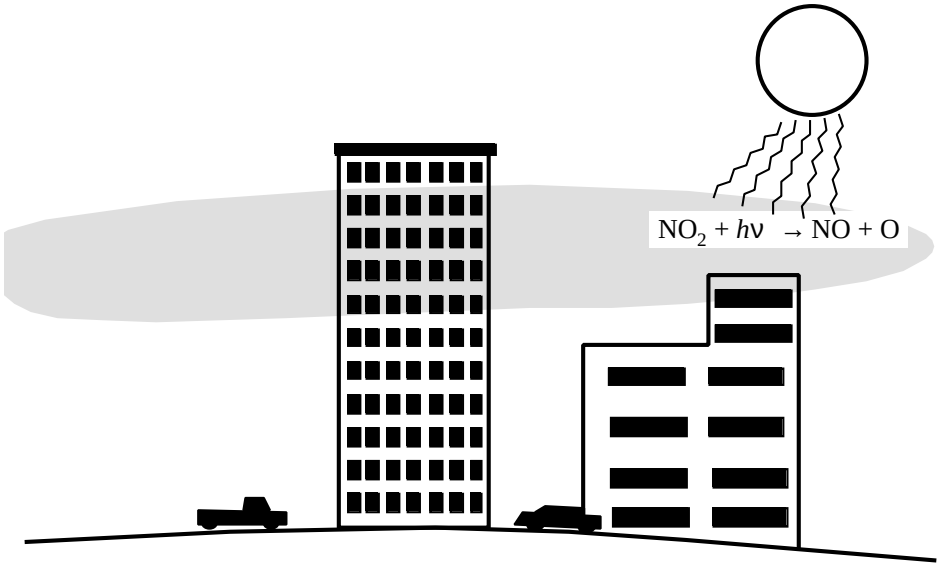


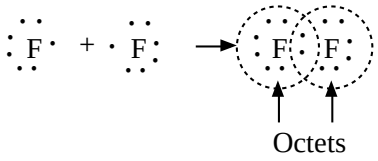
Figure 4.1 Breakage of a chemical bond between N and O in NO_2 starts the process involving a series of many reactions leading to the formation of unhealthy pollutant photochemical smog.

4.2 CHEMICAL BONDING AND THE OCTET RULE

The octet rule for chemical bonding was mentioned briefly in Chapter 3. At this point, it will be useful to examine the octet rule in more detail. Although there are many exceptions to it, the octet rule remains a valuable concept for an introduction to chemical bonding.

The Octet Rule for Some Diatomic Gases

Recall that some elemental gases—hydrogen, nitrogen, oxygen, and fluorine—do not consist of individual atoms, but of *diatomic molecules* of H_2, N_2, O_2, and F_2, respectively. This can be explained by the tendencies of these elements to attain a noble gas outer electron configuration. The bonds in molecules of F_2 are shown by the following:



(4.2.1)

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It is seen that the F_2 molecule is held together by a *single covalent bond* consisting of 2 shared electrons. As shown by the circles around them, each atom in the molecules has 8 outer electrons, some of them shared. These 8 electrons constitute an *octet* of outer electrons. Such an octet is possessed by the neon atom, which is the noble gas nearest to F in the periodic table.

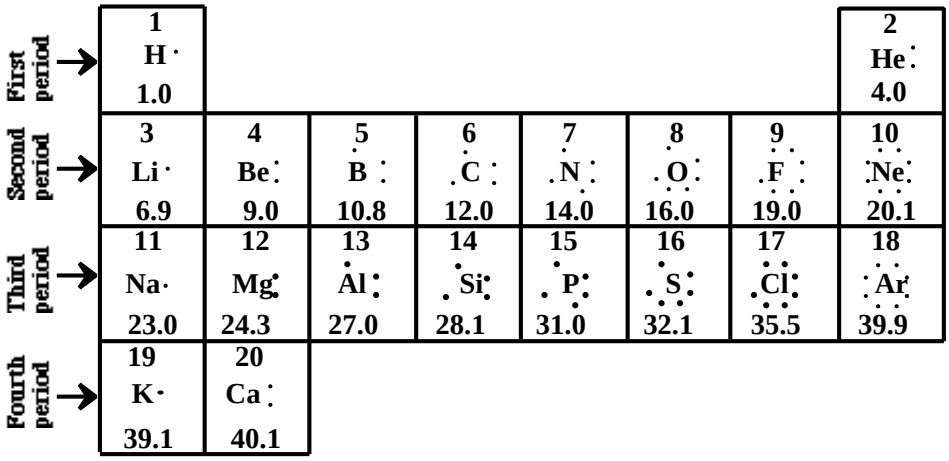


Figure 4.2 Abbreviated version of the periodic table showing outer shell (valence) electrons as dots. Electron configurations are also given.

The Octet Rule for Chemical Compounds

The octet rule illustrated for molecules of diatomic elemental fluorine above applies to molecules of chemical compounds. Recall from Section 1.4 that a *chemical compound* is formed from atoms or ions of two or more elements joined by chemical bonds. In many cases, compound formation enables elements to attain a noble gas electron configuration, usually an octet of outer shell electrons.

The most straightforward way for atoms to gain a stable octet is through loss and gain of electrons to form ions. This may be illustrated by the ionic compound sodium chloride as shown in Figure 4.3. By considering the Lewis symbols of Na

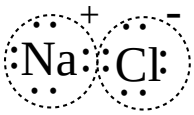


Figure 4.3 In the ionic compound NaCl, both the Na^+ ion and the Cl^- ion have octets of outer shell electrons. The Na^+ ion is formed by the loss of 1 electron from a sodium atom (see Figure 4.2) and the Cl^- ion is formed by a Cl atom gaining an electron.

and Cl atoms in Figure 4.2, it is easy to see that the octet of the Na^+ ion is formed by the loss of an electron from an Na atom and that of the Cl^- ion is produced by a Cl atom gaining 1 electron.

Normally, atoms of elements in the middle of a period of the periodic table, such as those of carbon or nitrogen atoms, share electrons to form *covalent bonds.* In methane, CH_4, each of 4 H atoms shares an electron with 1 C atom giving each C

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atom an 8-electron outer shell (octet) like neon. Each H atom has 2 electrons, both shared with C, which provides a shell of 2 electrons like that in the noble gas helium.

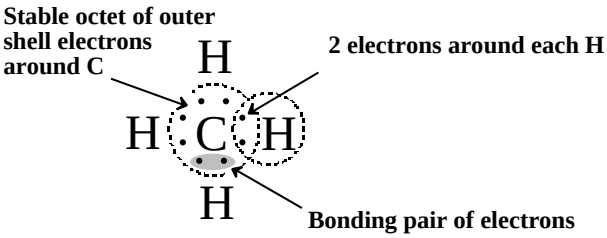


Figure 4.4 Stable outer electron shells from covalent bonding in compounds.

4.3 IONIC BONDING

An **ion** consists of an atom or group of atoms having an unequal number of electrons and protons and, therefore, a net electrical charge. A **cation** has a positive charge and an **anion** has a negative charge. The simplest kind of ion to visualize is one formed by the loss or gain by an atom of one or more electrons. As examples, loss of 2 electrons from a calcium atom gives the Ca^{2+} cation, and the gain of an electron by a Cl atom gives a Cl^- anion. An **ionic compound** is one that contains cations and anions. Such a compound is held together by **ionic bonds** that result from the mutual attraction of positively charged cations and negatively charged anions.

Electron Configurations of Ions from a Single Atom

Electron configurations of atoms were discussed in some detail in Chapter 3. Emphasis has been placed on the stability of a stable *octet* of outer shell electrons, which is characteristic of a *noble gas*. Such an octet is in the $\mathbf{ns^2np^6}$ electron configuration. The first element to have this configuration is neon, electron configuration $1s^22s^22p^6$. (Recall that helium is also a noble gas, but with only 2 electrons, its electron configuration is simply $1s^2$). The next noble gas beyond neon is argon, which has the electron configuration $1s^22s^22p^63s^23p^6$ commonly abbreviated $\{Ne\}3s^23p^6$.

The electron configurations of ions consisting of only one atom can be shown in the same way as illustrated for atoms above. For the lighter elements, the electron configurations are those of the nearest noble gas. Therefore, in forming ions, an atom of an element that is just before a particular noble gas in the periodic table *gains* enough electrons to get the configuration of that noble gas, whereas an atom of an element just beyond a noble gas *loses* enough electrons to attain the electron configuration of the nearest noble gas. This is best seen in reference to the periodic table showing electron configurations as seen in Figure 4.2.

As an example of electron configurations of ions, consider an anion, F^-, and a cation, Mg^{2+}, both near neon in the periodic table. From Figure 4.2, it is seen that the electron configuration of the neutral fluoride atom is $1s^22s^22p^5$. To get the stable

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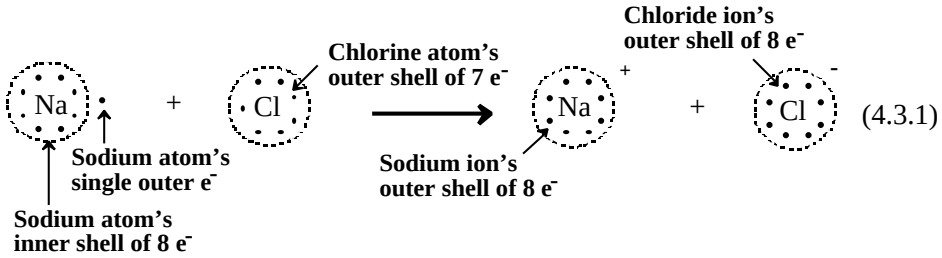
noble gas electron configuration of neon, the fluoride atom may gain 1 electron to become F^- ion, electron configuration $1s^2 2s^2 2p^6$. The electron configuration of magnesium, atomic number 12, is $1s^2 2s^2 2p^6 3s^2$. A magnesium atom can attain the stable electron configuration of neon by losing its 2 outer shell 3*s* electrons to become Mg^{2+} ion, electron configuration $1s^2 2s^2 2p^6$. The electron configurations of some other ions near neon and argon in the periodic table are given in Table 4.1.

Table 4.1 Ions with Neon and Argon Electron Configurations

Element[1]	Electron configuration	Electrons gained/lost	Ion	Ion electron configuration	
N (7)	$1s^2 2s^2 2p^3$	Gain 3 *e*-	N^{3-}	$1s^2 2s^2 2p^6$	Neon
O (8)	$1s^2 2s^2 2p^4$	Gain 2 *e*-	O^{2-}	$1s^2 2s^2 2p^6$	
F (9)	$1s^2 2s^2 2p^5$	Gain 1 *e*-	F^-	$1s^2 2s^2 2p^6$	
Na (11)	$1s^2 2s^2 2p^6 3s^1$	Lose 1 *e*-	Na^+	$1s^2 2s^2 2p^6$	
Mg (12)	$1s^2 2s^2 2p^6 3s^2$	Lose 2 *e*-	Mg^{2+}	$1s^2 2s^2 2p^6$	
S (16)	$1s^2 2s^2 2p^6 3s^2 3p^4$	Gain 2 *e*-	S^{2-}	$1s^2 2s^2 2p^6 3s^2 3p^6$	Argon
Cl (17)	$1s^2 2s^2 2p^6 3s^2 3p^5$	Gain 1 *e*-	C^-	$1s^2 2s^2 2p^6 3s^2 3p^6$	
K (19)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	Lose 1 *e*-	K^+	$1s^2 2s^2 2p^6 3s^2 3p^6$	
Ca (20)	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	Lose 2 *e*-	Ca^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6$	

Sodium Chloride as an Ionic Compound

The formation of sodium chloride, NaCl, is often cited as an example of the production of an ionic compound and its constituent ions, and the stable octets of Na^+ and Cl^- ions were shown in Figure 4.3. Here the nature of sodium chloride as an ionic compound is considered in more detail. The electron configurations of both Na^+ ion and Cl^- ion are given in Table 4.1. The reaction between a neutral elemental sodium atom and a neutral elemental chlorine atom to form NaCl consisting of Na^+ and Cl^- ions is as follows:



(4.3.1)

A compound such as NaCl that is composed of ions is an ionic compound. The ionic bonds in such a compound exist because of the electrostatic attraction between ions of opposite charge. An ionic compound possesses a crystal structure such that a particular ion is located as close as possible to attracting ions of opposite charge and as far as possible from repelling ions with the same charge. Figure 4.5 shows such a structure for NaCl. Visualized in three dimensions, this figure shows how the six nearest neighbors of each ion are ions of opposite charge. Consider the Cl^- ion with

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the arrow pointing to it in the center of the structure. Every line intersecting the sphere that represents the Cl^- ion leads to a nearest neighbor ion, each of which is an Na^+ ion. The closest Cl^- ions are actually farther away than any of the six nearest neighbor Na^+ ions. The crystal structure is such that each Na^+ ion is similarly surrounded by six nearest neighbor Cl^- ions. Therefore, every ion in the crystal is closest to ions of opposite charge resulting in forces of attraction that account for the stability of ionic bonds. Depending upon the relative numbers of cations and anions in a compound and upon their sizes, there are various crystalline structures that maximize the closeness of ions of opposite charge and, therefore, the strengths of ionic bonds. Although the ball and stick model in Figure 4.5 shows the relative positions of the ions, the ions are actually considered to be of a size such that they fill the spaces in the structure and touch each other (the Cl^- ion is larger than the Na^+ ion, as shown in Figure 4.7).

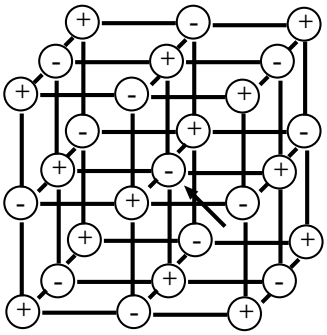


Figure 4.5 Representation of the structure of NaCl. This structure can be visualized in three dimensions as "balls" with interconnecting "sticks." The balls are Na^+ and Cl^- ions with the charges designated.

Energetics in Ionic Bonding

The stability of the ionic bond is the result of the interaction of several factors involving the energetics of the attraction of atoms for electrons and of oppositely charged ions for each other. To understand some of the factors involved, consider the reaction of isolated gas-phase atoms of Na and Cl to form solid NaCl. This is a somewhat simplified view in that it does not take account of the fact that sodium is a solid under normal conditions and that elemental chlorine exists as diatomic molecules of Cl_2; when solid Na and gaseous Cl_2 react, energy is involved in removing Na atoms from the elemental solid, as well as in breaking the covalent bond between Cl atoms in Cl_2. The reaction to be considered is the following:

$$Na\cdot(g) + \cdot\ddot{\underset{\cdot\cdot}{Cl}}:(g) \rightarrow Na^+ + :\ddot{\underset{\cdot\cdot}{Cl}}:^-(g) \rightarrow Na^+:\ddot{\underset{\cdot\cdot}{Cl}}:^-(s) \qquad (4.3.2)$$

When gas-phase sodium and chlorine atoms react, *ionization energy* is involved in the removal of an electron from a sodium atom to form Na^+, *electron affinity* is involved in the addition of an electron to a chlorine atom to produce Cl^-, and *lattice energy* is released by oppositely charged ions coming together in the sodium chloride crystal.

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Three energy changes are listed for the process outlined in the above equation. These are the following:

- Even though the sodium ion has been represented as being "willing" to lose its valence electron to attain a noble gas electron configuration, some energy is required. This is called the **ionization energy**. In the case of sodium, the ionization energy for the removal of the single outer shell electron is +490 kJ/mole. The positive value indicates that energy must be put into the system to remove the electron from Na. For each mole of Na atoms, the amount of energy is 490 kilojoules.

- When an electron is added to a Cl atom, the energy is expressed as **electron affinity**, with a value of -349 kJ/mole. The negative sign denotes that energy is *released*; for the addition of 1 electron to each atom in a mole of Cl atoms, 349 kJ of energy is evolved.

- A very large amount of energy is released when a mole of solid NaCl is formed by a mole of Na^+ and a mole of Cl^- ions coming together to form a **crystal lattice** of ions arranged in a crystalline structure. The energy change for this process is -785 kJ/mole.

The net energy change for Reaction 4.3.2 is given by the following:

Energy change =	Ionization energy for Na(*g*)	+ Electron affinity of Cl(*g*)	+ Energy released by Na^+ and Cl^- coming together to form NaCl(*s*)	(4.3.3)
=	490 kJ	-349 kJ	-785kJ	
=	-644 kJ			

This calculation shows that when 1 mole of solid NaCl is formed from 1 mole each of gas-phase Na and Cl atoms, the energy change is -644 kilojoules; the negative sign shows that energy is released, so that the process is energetically favored. Under normal conditions of temperature and pressure, however, sodium exists as the solid metal, Na(*s*), and chlorine is the diatomic gas, Cl_2(s). The reaction of 1 mole of solid sodium with one mole of chlorine atoms contained in gaseous Cl_2 to yield 1 mole of NaCl is represented by,

$$Na(s) + {}^1/_2\, Cl_2(g) \rightarrow NaCl(g) \qquad (4.3.4)$$

The energy change for this reaction is -411 kJ/mole, representing a significantly lower release of energy from that calculated in Equation 4.3.3. This difference is due to the energy used to vaporize solid Na and to break the Cl-Cl bonds in diatomic Cl_2. The total process for the formation of solid NaCl from solid Na and gaseous Cl_2 is outlined in Figure 4.6, a form of the Born-Haber cycle.

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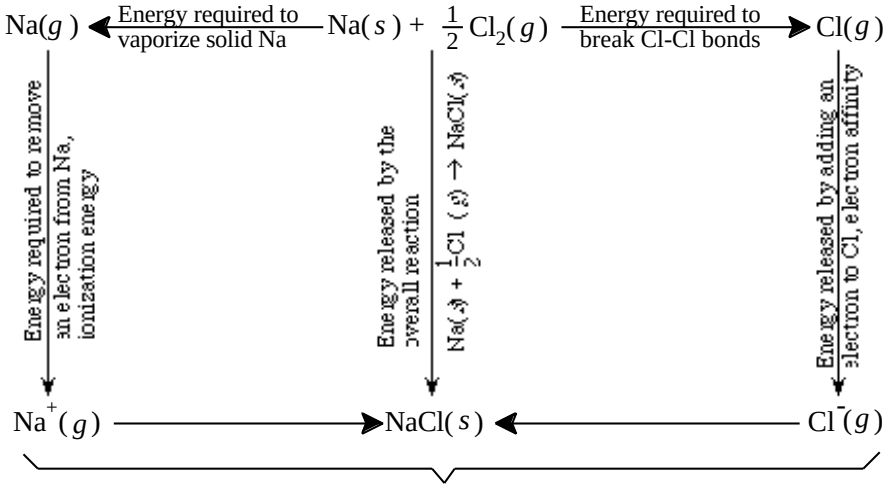


Figure 4.6 Energy changes involved in the formation of an ionic compound from its constituent elements. The overall process is shown by the vertical arrow in the middle and the constituent parts by the arrows around the periphery.

Energy of Ion Attraction

In the case of NaCl, it is seen that the largest component of the energy change that occurs in the formation of the ionic solid is that released when the ions come together to form the solid. This may be understood in light of the potential energy of interaction, E, between two charged bodies, given by the equation,

$$E = k\frac{Q_1Q_2}{d} \tag{4.3.5}$$

where Q_1 and Q_2 are the charges on the two bodies in coulombs, d is the distance between their centers in meters, and k is a constant with a value of 8.99×10^9 J-m/C^2. If one of the bodies has a + and the other a - charge, as is the case with oppositely charged ions, the sign of E is negative, consistent with the fact that energy is released when oppositely charged bodies come together. The magnitude of E is greater for larger values of Q_1 and Q_2 (higher ionic charges, such as the 2+ for Ca^{2+} ion compared with the 1+ for Na^+ ion) and greater for smaller values of d (smaller radii of ions allowing them to approach more closely).

Lattice Energy

Having considered the energy of interaction between charged particles, next consider the large amount of energy involved with the packing of ions into a crystalline lattice. The lattice energy for a crystalline ionic compound is that required to separate all of the ions in the compound and remove them a sufficient distance from each other so that there is no interaction between them. Since energy input is required to do this for ionic compounds, lattice energy has a positive value; it is conventionally expressed in kilojoules per mole of compound. For the example being considered,

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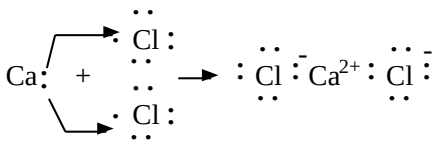
the lattice energy of NaCl is +785 kJ/mole. However, in considering the production of an ionic compound, as shown in Reaction 4.3.3, the opposite process was considered, which is the assembling of a mole of Na^+ ions and a mole of Cl^- ions to produce a mole of solid NaCl. This releases the lattice energy, so that its contribution to the energy change involved was given a minus sign, that is, -785 kJ/mole.

Ion Size

Equation 4.3.5 shows that the distance between the centers of charged bodies, d, affects their energy of interaction. For ionic compounds this is a function of ionic size; smaller ions can get closer and therefore, their energies of interaction as measured by lattice energy are greater. Because of the removal of their outer shell electrons, cations are smaller than the atoms from which they are formed; because of the addition of outer shell electrons, anions are larger than their corresponding neutral atoms. Some ion sizes are shown in Figure 4.7. This figure shows some trends in ion size across periods of the periodic table and within vertical groups in the table. In going from left to right across a period, it is seen that the cations decrease in size with increasing ionic charge. The size of cations within a period decreases significantly in the order of 1+, 2+, and 3+ ions. There is a large increase in ion size as anions are formed. The doubly charged anions within a period are larger than the singly charged ones. For example, the O^{2-} ion is larger than the F^- ion as shown in Figure 4.7.

Formation of Some Example Ionic Compounds

Next consider several other ionic compounds that contain some of the ions shown in Figure 4.7. To better illustrate the transfer of electrons, these are shown for the formation of ions from single atoms, even in cases where diatomic gases are involved. Calcium and chlorine react,



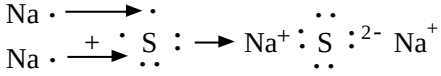
(4.3.6)

to form calcium chloride, $CaCl_2$. This compound is a byproduct of some industrial processes and is used to salt "icy" streets, causing the ice to melt and, unfortunately, automobiles to rust. The reaction of magnesium and oxygen,



(4.3.7)

yields magnesium oxide, MgO. This compound is used in heat-resistant refractory materials (such as those used to line industrial furnaces), insulation, cement, and paper manufacture. Sodium and sulfur react,



(4.3.8)

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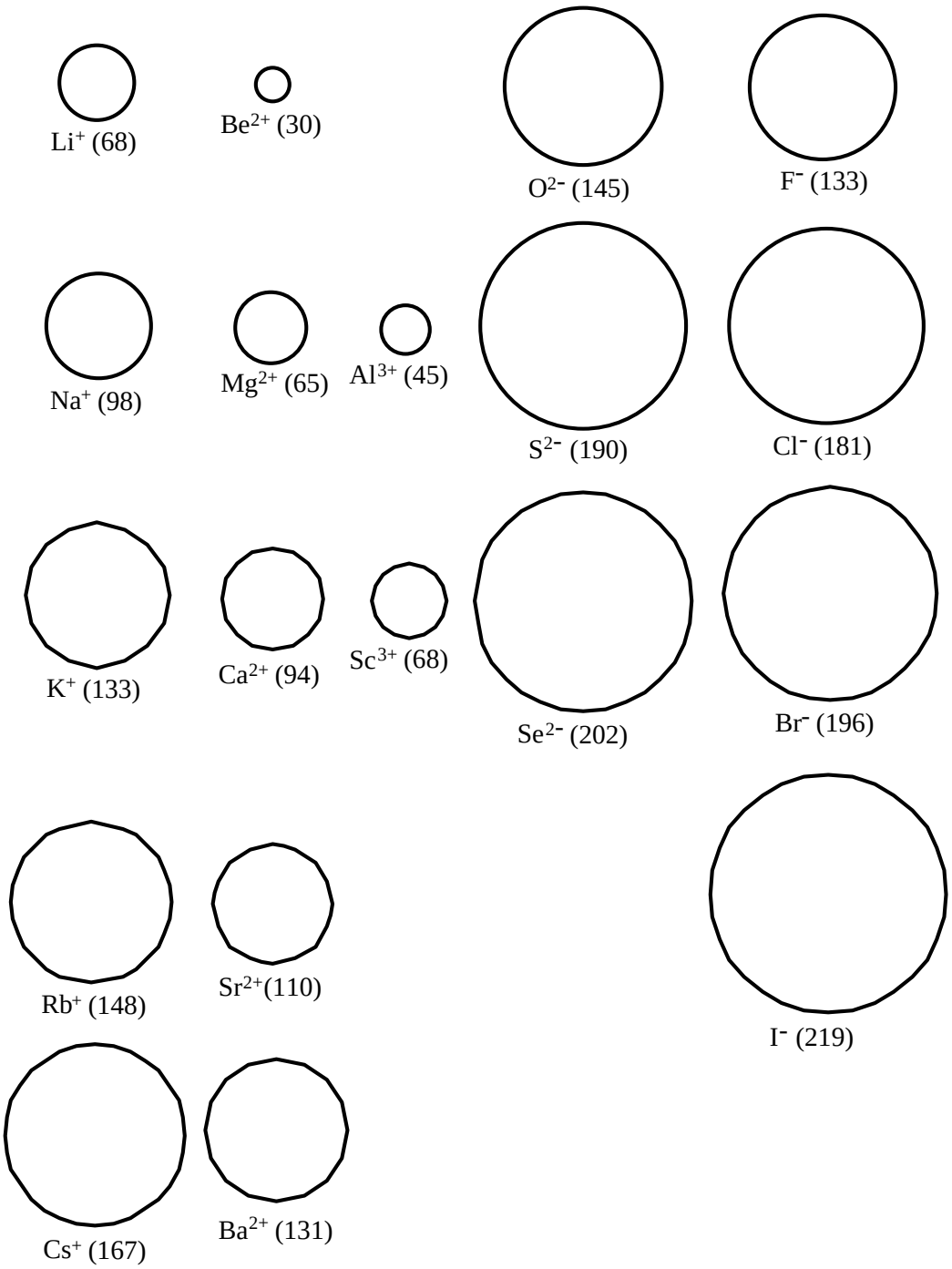
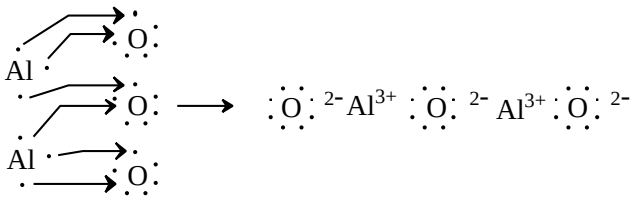


Figure 4.7 Diameters of some ions formed from single atoms, units of picometers (1 Ångstrom = 100 pm)

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to yield sodium sulfide, Na_2S. Among its other uses, this ionic compound is an intermediate in one of the processes used in wood pulping for paper manufacture. As a final example, consider the following reaction of aluminum and oxygen:



(4.3.9)

The product, aluminum oxide, $A1_2O_3$, is the most widely used aluminum compound. It is commonly called alumina. Among the products that it is used to make are abrasives, ceramics, antacids, and antiperspirants.

Exercise: Fill in the table below for the ionic products of the reaction of the metal and nonmetal indicated.

Metal	Nonmetal	Cation formed	Anion formed	Ionic compound
Li	Cl	(a)_____	(b)_____	(c)_____
K	S	(d)_____	(e)_____	(f)_____
Ca	F	(g)_____	(h)_____	(i)_____
Ba	O	(j)_____	(k)_____	(l)_____
Ca	N	(m)_____	(n)_____	(o)_____

Answers: (a) Li^+, (b) Cl^-, (c) LiCl, (d) K^+, (e) S^{2-}, (f)K_2S, (g) Ca^{2+}, (h) F^-, (i) CaF_2, (j) Ba^{2+}, (k) O^{2-}, (l) BaO, (m) Ca^{2+}, (n) N^{3-}, (o) Ca_3N_2

4.4 FUNDAMENTALS OF COVALENT BONDING

Chemical Bonds and Energy

The energy changes involved in the formation of ions and ionic compounds were mentioned prominently in the preceding discussion of ionic compounds. In fact, bonds form largely as the result of the tendency of atoms to attain minimum energy. Several kinds of bonds are possible between atoms, and energy considerations largely determine the type of bonds that join atoms together. It was shown in the preceding section that *ionization energy*, *electron affinity*, and *lattice energy* are all strongly involved in forming ionic bonds. Ionic compounds form when the sum of the energy released in forming anions (electron affinity) and in the cations and anions coming together (lattice energy) is sufficient to remove electrons from a neutral atom to produce cations (ionization energy). It was seen that, for simple monatomic ions, conditions are most likely to be favorable for the formation of ionic bonds when the cations are derived from elements on the left side of the periodic table and the anions from those near the right side. In addition, the transition elements can lose 1–3 electrons to form simple monatomic cations, such as Cu^+, Zn^{2+}, and Fe^{3+}.

In many cases, however, the criteria outlined above are not energetically favorable for the formation of ionic bonds. In such cases, bonding can be accom-

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plished by the sharing of electrons in covalent bonds. Whereas oppositely charged ions attract each other, neutral atoms have a tendency to repel each other because of the forces of repulsion between their positively charged nuclei and the negatively charged clouds of electrons around the nuclei. Sharing electrons in covalent bonds between atoms enables these forces of repulsion to be overcome and results in energetically favored bonding between atoms. Covalent bonding is discussed in this and following sections.

Covalent Bonding

A **covalent bond** is one that joins 2 atoms through the sharing of 1 or more pairs of electrons between them. Covalent bonds were discussed briefly in Chapter 1. The simplest such bond to visualize is that which forms between 2 hydrogen atoms, to yield a diatomic molecule of hydrogen, H_2:

$$H^{\bullet} \quad + \quad {}^{\bullet}H \longrightarrow H{:}H \qquad (4.4.1)$$

Figures 4.8 and 4.9 illustrate some important characteristics of the H-H bond. As shown in Figure 4.8, there is an electron cloud between the 2 positively charged H atom nuclei. This is the covalent bond consisting of a pair of shared electrons that holds the 2 atoms together. Figure 4.9 is an energy diagram for the H_2 molecule. The 2 hydrogen nuclei are shown at the distance that results in minimum energy, the bond length. Forcing the nuclei close together results in rapidly increasing energy because of the repulsive forces between the nuclei. The energy increases more gradually with distances farther apart than the bond length, approaching zero energy as complete separation is approached. The bond energy of 435 kJ/mol means that a total energy of 435 kilojoules is required to break all the bonds in a mole of H_2 molecules and totally separate the resulting H atoms.

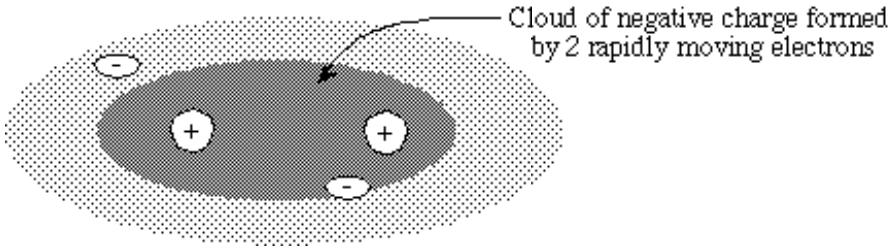


Figure 4.8 Two hydrogen nuclei, +, covalently bonded together by sharing 2 electrons, -. The negatively charged cloud of electrons is concentrated between the 2 nuclei, reducing their natural tendency to repel each other.

4.5 COVALENT BONDS IN COMPOUNDS

Consider next some example covalent bonds between atoms of some of the lighter elements. These are best understood in reference to Figure 4.2, the abbreviated version of the periodic table showing the Lewis symbols (outer shell valence electrons) of the first 20 elements. As is the case with ions, atoms that are covalently bonded in molecules often have an arrangement of outer shell electrons

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like that of the noble gas with an atomic number closest to the element in question. It was just seen that covalently bonded H atoms in molecules of H_2 have 2 outer shell electrons like the nearby noble gas helium. For atoms of many other elements, the tendency is to acquire 8 outer shell electrons—an octet—in sharing electrons through covalent bonds. This tendency forms the basis of the *octet rule* discussed in Section 4.2. In illustrating the application of the octet rule to covalent bonding consider first the bonding of atoms of hydrogen to atoms of elements with atomic numbers 6 through 9 in the second period of the periodic table. These elements are close to the noble gas neon and tend to attain a "neon-like" octet of outer shell electrons when they form covalently bonded molecules.

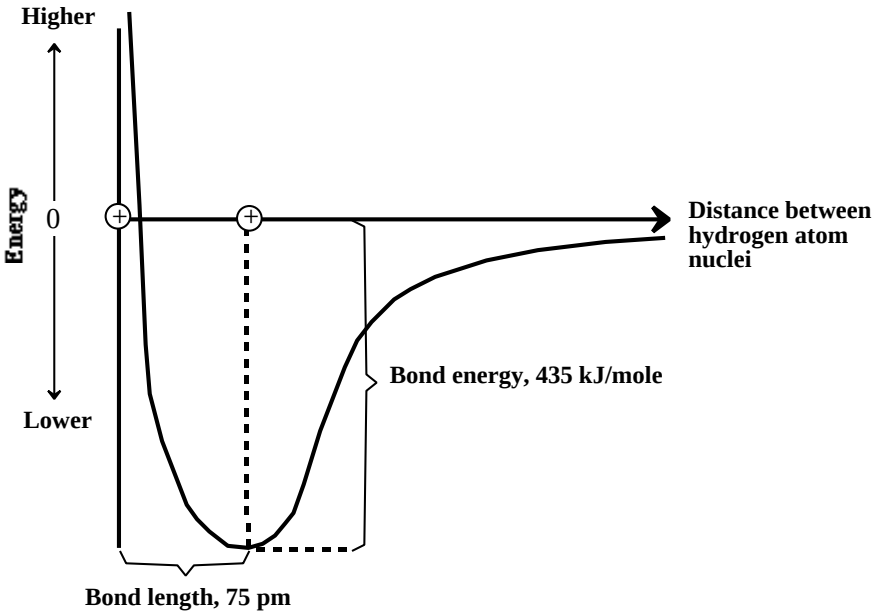


Figure 4.9 Relationship between energy and distance between hydrogen nuclei (energy diagram of H_2). The nuclei are shown at the most energetically favored distance apart, that is, the bond length of the H_2 atom.

As shown in Figure 4.10, when each of the 4 H atoms shares an electron with 1 C atom to form a molecule of methane, CH_4, each C atom attains an 8-electron outer shell (octet) like neon. Every hydrogen atom attains an outer shell of 2 electrons through the arrangement of shared electrons. There is a total of 4 covalent bonds, 1 per H attached to the C atom, and each composed of a shared pair of electrons. Each of the hydrogen atoms has 2 electrons like the noble gas helium and carbon has an octet of outer shell electrons like the noble gas neon.

Also shown in Figure 4.10, nitrogen bonds with hydrogen such that 1 N atom shares 2 electrons with each of 3 H atoms to form a molecule of ammonia, NH_3. This arrangement gives the N atom 8 outer shell electrons, of which 6 are shared with H atoms and 2 constitute an **unshared pair** of electrons. In both CH_4 and NH_3, each H atom has 2 shared electrons, which provides a shell of 2 electrons like that in the noble gas helium.

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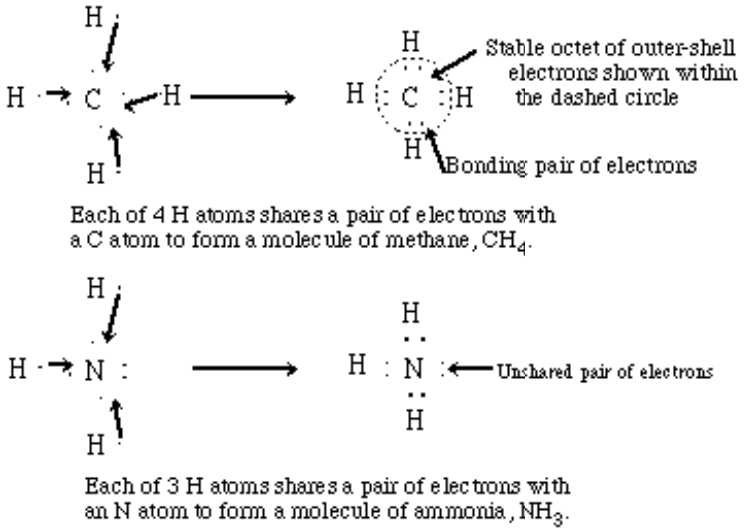


Figure 4.10 Formation of stable outer electron shells by covalent bonding in compounds.

In discussing covalent bonds and molecules it is sometimes convenient to use the term **central atom** in reference to an atom to which several other atoms are bonded. In the case of CH_4 which was just discussed, C is the central atom. For NH_3 nitrogen, N, is the central atom.

The use of Lewis symbols and formulas in the preceding examples readily shows how many atoms are bound together in each of the compounds and the types of bonds in each. The products of each reaction are shown in two ways, one in which all the valence electrons are represented as dots, and the other in which each pair of valence electrons in a chemical bond is shown as a dash, and the unbonded valence electrons as dots. In cases where all that is needed is to show which atoms are bonded together and the types of bonds (one dash for a single covalent bond, two for a double bond of 2 shared electron pairs, and three for a triple bond of 3 shared electron pairs), the dots representing unshared electrons may be omitted.

Figure 4.11 shows covalent bonding in the formation of hydrogen compounds of O and F. In the case of oxygen, 2 H atoms are combined with 1 O atom having 6 valence electrons, sharing electrons such that each H atom has 2 electrons and the

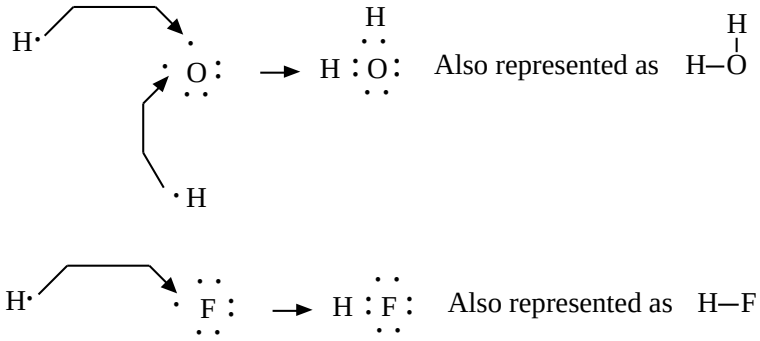


Figure 4.11 Covalent bonding of H to O and F to produce H_2O and HF, respectively.

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O atom has 8 outer shell electrons, 4 of which are in 2 shared pairs. To form HF, only 1 H atom is required to share its electron with an atom of F having 7 outer shell electrons, leading to a compound in which the F atom has 8 outer shell electrons, 2 of which are shared with H.

Of the compounds whose formation is shown above, CH_4 is methane, the simplest of the hydrocarbon compounds and the major component of natural gas. The compound formed with nitrogen and hydrogen is ammonia, NH_3. It is the second most widely produced synthetic chemical, a pungent-smelling gas with many uses in the manufacture of fertilizer, explosives, and synthetic chemicals. The product of the reaction between hydrogen and oxygen is, of course, water, H_2O. (Another compound composed only of hydrogen and oxygen is hydrogen peroxide, H_2O_2, a reactive compound widely used as a bleaching agent). Hydrogen fluoride, HF, is the product of the chemical combination of H and F. It is a toxic corrosive gas (boiling point 19.5°C) used as a raw material to manufacture organofluorine compounds and Teflon plastics.

Having seen how hydrogen combines with carbon, nitrogen, oxygen, and fluorine, it is easy to predict the hydrogen compounds with the elements directly below C, N, O, and F in the third period of the periodic table. These elements are silicon, phosphorus, sulfur, and chlorine, atomic numbers 14 through 17. As shown in Figure 4.12, these elements combined with hydrogen have covalent bonds such that every hydrogen atom has 2 outer shell electrons and each of the other elements has an octet of outer shell electrons.

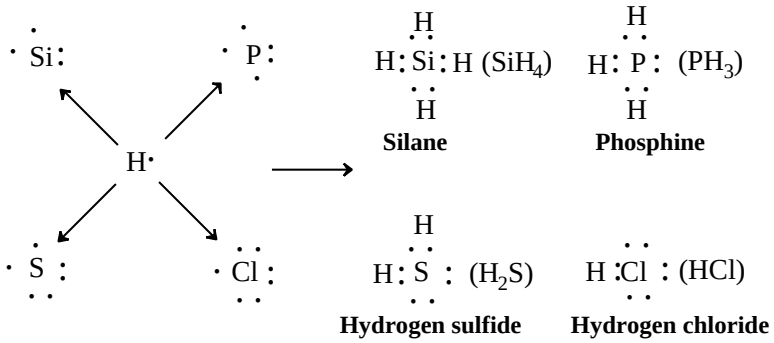


Figure 4.12 Chemical compounds of Si, P, S, and Cl with H.

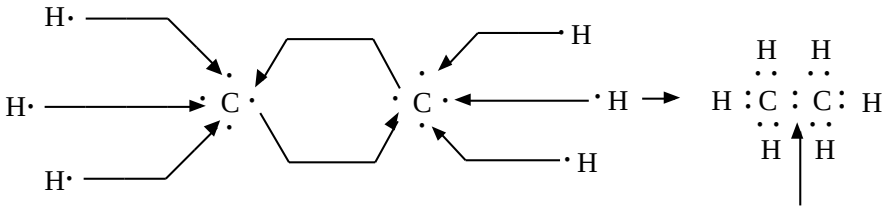
Silane, SH_4, is a colorless gas. **Phosphine**, PH_3 is also a gas; it catches fire spontaneously when exposed to air, is very toxic, and has a bad odor. **Hydrogen sulfide**, H_2S, is a toxic gas with a foul, rotten-egg odor. Natural gas contaminated with hydrogen sulfide is said to be sour, and the hydrogen sulfide must be removed before the natural gas can be used as a fuel. Fortunately, H_2S is readily converted to elemental sulfur or to sulfuric acid, for which there are ready markets. **Hydrogen chloride** gas has a sharp odor and is very soluble in water. Solutions of hydrogen chloride in water are called **hydrochloric acid**. About 2.5 million tons of hydrochloric acid are produced for industrial applications in the U.S. each year.

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4.6 SOME OTHER ASPECTS OF COVALENT BONDING

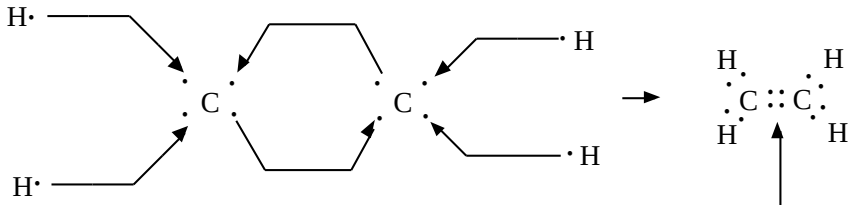
Multiple Bonds and Bond Order

Several examples of single bonds consisting of a pair of shared electrons have just been seen. Two other types of covalent bonds are the *double bond* consisting of two shared pairs of electrons (4 electrons total) and the *triple bond* made up of three shared pairs of electrons (6 electrons total). These are both examples of **multiple bonds**. Examples of a double bond in ethylene and of a triple bond in acetylene are shown in Figure 4.13.



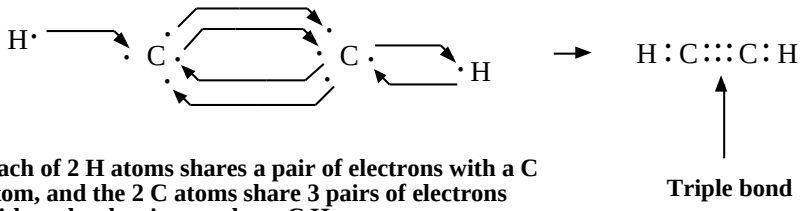
Each of 6 H atoms shares a pair of electrons with a C atom, and the 2 C atoms share a pair of electrons between each other in ethane, C_2H_6.

Single bond



Each of 4 H atoms shares a pair of electrons with a C atom, and the 2 C atoms share 2 pairs of electrons between each other in ethylene, C_2H_4.

Double bond



Each of 2 H atoms shares a pair of electrons with a C atom, and the 2 C atoms share 3 pairs of electrons with each other in acetylene, C_2H_2.

Triple bond

Figure 4.13 Single, double, and triple bonds between C atoms in three different hydrocarbon molecules, each of which contains 2 C atoms.

Atoms of carbon, oxygen, and nitrogen bonded to each other are the most likely to form multiple bonds. In some cases, sulfur forms multiple bonds. Multiple bonds are especially abundant in the functional groups of organic compounds (Chapter 9).

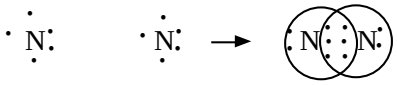
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Lengths and Strengths of Multiple Bonds

In various compounds, bonds between the same two atoms (either of the same or different elements) may be single, double, or triple. This is seen below for the three types of carbon–carbon bonds illustrated in Figure 4.13:

Bond type:	Single in C_2H_6	Double in C_2H_4	Triple in C_2H_2
Bond length:	154 pm (pm stands for picometers)	134 pm	120 pm
Bond strength:	348 kJ/mol	614 kJ/mol	839 kJ/mol

The above shows that as the bond multiplicity increases, the bonds become shorter. Furthermore, the bond strength, expressed as the energy in kilojoules needed to break a mole of the bonds, increases. These trends are reasonable if a covalent bond is viewed as consisting of electrons located between the two atoms that are bonded together, such that the positively charged nuclei of the atoms are attracted to the electrons in the bond. Increasing multiplicity gives a denser cloud of electrons, enabling the atoms to approach closer and resulting in shorter bond length. The same reasoning explains the greater strength of multiple bonds. One of the strongest common bonds is the triple N≡N bond in molecular nitrogen, N_2:



(4.6.1)

The number of bonding electron pairs that make up the bond between two atoms is called the **bond order**. The single, double, and triple bonds described above have bond orders of 1, 2, and 3, respectively. It was just shown that bond strength increases and bond length decreases with increasing numbers of electrons in the bonds connecting two atom nuclei. Therefore, increased bond order is associated with increased bond energy and decreased bond length. These relationships were illustrated above for C-C, C=C, and C≡C bonds.

The absorption of infrared radiation by bonds in molecules provides the chemist with a powerful probe to determine bond orders, lengths, and energies. Infrared radiation was mentioned as a form of electromagnetic radiation in Chapter 3. When absorbed by molecules, infrared energy causes atoms to vibrate and (when more than 2 atoms are present) bend relative to each other. The chemical bond can be compared to a spring connecting 2 atomic nuclei. A short, strong bond acts like a short, strong spring, so that the atoms connected by the bond vibrate rapidly relative to each other. The infrared radiation absorbed by the bond causes it to vibrate. For a particular mode of bond vibration, the infrared radiation absorbed must be of a specific energy, which results in specific frequencies (ν) and wavelengths (λ) for the infrared radiation absorbed (see Section 3.11 in Chapter 3 for the relationships among energies, frequencies, and wavelengths of electromagnetic radiation).

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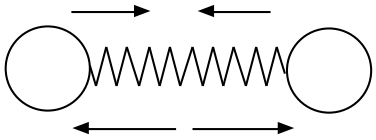


Figure 4.14 Representation of vibration of a chemical bond as a spring connecting 2 atom nuclei (circles).

Electronegativity and Covalent Bonding

Electronegativity refers to the ability of a bonded atom to attract electrons to itself. Whereas the previously discussed ionization energy and electron affinity deal with the attraction for electrons of isolated gas-phase atoms, electronegativity applies to bonded atoms. Tabulated values of electronegativity range from 0.79 for cesium to 4.0 for fluorine. Unlike ionization energies and electron affinities, which are directly measurable intrinsic properties of atoms, electronegativities are numerical estimates calculated from several elemental properties. Electronegativity values for the first 20 elements are shown in Figure 4.15.

1 H 2.2							2 He -
3 Li 1.0	4 Be 1.6	5 B 1.8	6 C 2.5	7 N 3.0	8 O 3.4	9 F 4.0	10 Ne -
11 Na 0.93	12 Mg 1.3	13 Al 1.6	14 Si 1.9	15 P 2.2	16 S 2.6	17 Cl 3.2	18 Ar -
19 K 0.82	20 Ca 1.0						

Figure 4.15 Electronegativities of the first 20 elements in the periodic table.

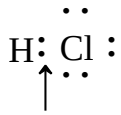
Examination of Figure 4.15 shows that electronegativity values increase from left to right across a period of the periodic table (there is little discernible trend for the transition elements). Within a group of elements, electronegativity decreases with increasing atomic number. For the elements in the abbreviated version of the periodic table shown, this is most obvious for the active metals in the first two groups.

As will be seen in the next section, electrons are often shared unequally between atoms in chemical bonds. The electronegativity concept is useful in dealing with this important phenomenon in chemical bonding.

Sharing Electrons—Unequally

The Lewis formula for hydrogen chloride, HCl, is illustrated at the top of the following page:

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Shared electron pair in covalent bond

This formula might leave the impression that the two electrons in the covalent bond between H and Cl are shared equally between the two atoms. However, the numbers in Figure 4.14 show that the electronegativity of Cl, 3.2, is significantly higher than that of H, 2.2. This indicates that the Cl atom has a greater attraction for electrons than does the H atom. Therefore, the 2 electrons shared in the bond spend a greater fraction of time in the vicinity of the Cl atom than they do around the H atom. The result of this unequal sharing of electrons is that the chloride end of the molecule acquires a partial negative charge and the hydrogen end a partial positive charge. Although the overall charge of the molecule is zero, it is distributed unequally over the molecule. A body with an unequal electrical charge distribution is said to be **polar**. A covalent bond in which the electrons are not shared equally is called a **polar covalent bond**. A covalent bond in which the sharing of electrons is exactly equal is a **nonpolar covalent bond**.



Electrons shared between two identical atoms are shared equally and the covalent bond is nonpolar.

The ultimate in unequal sharing of electrons is the ionic bond, in which there is a complete transfer of electrons.

The two common ways of showing a polar bond are illustrated below. The δs represent partial positive and partial positive charge; the point of the arrow is toward the more electronegative atom that attracts electrons more strongly than the other atom.

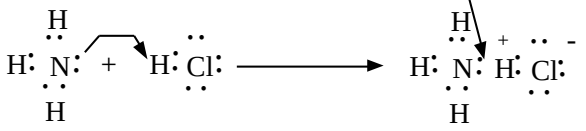


Coordinate Covalent Bonds

The covalent bonds examined so far have consisted of electrons contributed equally from both of the atoms involved in the bond. It is possible to have covalent bonds in which only 1 of the 2 atoms that are joined together contributes both of the electrons in the bond. The bond so formed is called a **coordinate covalent bond** or a **dative bond**. A typical coordinate covalent bond forms when ammonia gas and hydrogen chloride gas react. This sometimes happens accidentally in the laboratory when these gases are evolved from beakers of concentrated ammonia solution and concentrated hydrochloric acid (a solution of HCl gas) that are accidentally left uncovered. When these two gases meet, a white chemical fog is formed. It is ammonium chloride, NH_4Cl, a salt that is produced by the reaction shown at the top of the following page:

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Site of coordinate covalent bond formation (after the bond has formed, the four N-H bonds are identical)



(4.6.2)

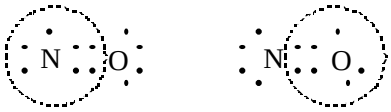
White solid ammonium chloride

in which the unshared pair of electrons from NH_3 forms a coordinate covalent bond with an H^+ ion released from HCl. The product is an ion of NH_4. After the coordinate covalent bond has formed, the ammonium ion has four equivalent N-H bonds; the one formed by coordinate covalent bonding is indistinguishable from the other three bonds.

Compounds that do not Conform to the Octet Rule

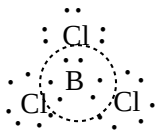
By now a number of examples of bonding have been shown that are explained very well by the octet rule. There are numerous exceptions to the octet rule, however. These fall into the three following major categories:

1. Molecules with an uneven number of valence electrons. A typical example is nitric oxide, NO. Recall that the nitrogen atom has 5 valence electrons and the oxygen atom 6, so that NO must have 11, an uneven number. The Lewis structure of NO may be represented as one of the two following forms (these are resonance structures, which are discussed later in this section):



Nitrogen atom has only 7 outer-shell electrons. **Oxygen atom has only 7 outer shell electrons.**

2. Molecules in which an atom capable of forming an octet has fewer than 8 outer electrons. A typical example is highly reactive, toxic boron trichloride, BCl_3.

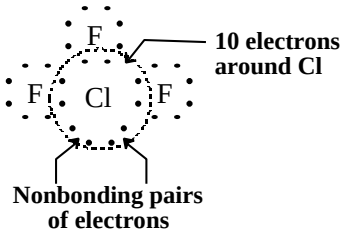


The dashed circle around the central B atom shows that it has only 6 outer shell electrons. However, it can accept 2 more from another compound such as NH_3 to fill a vacant orbital and complete an octet.

3. Molecules in which an atom has more than 8 outer electrons. This can occur with elements in the third and higher periods of the periodic table because of their underlying *d* orbitals capable of accepting electron pairs, so that the valence shell is no longer confined to one *s* orbital and

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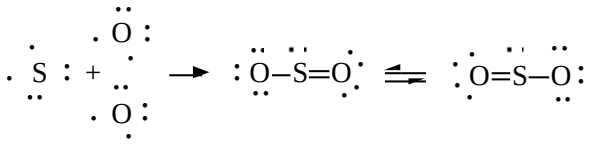
three *p* (orbitals that make up an octet of electrons). An example of a compound with more than 8 outer electrons is chlorine trifluoride,



composed of 4 halide atoms (Cl and F), each of which has 7 valence electrons for a total of 28. These are accommodated by placing 5 electron pairs—2 of them non-bonding—around the central Cl atom.

Resonance Structures

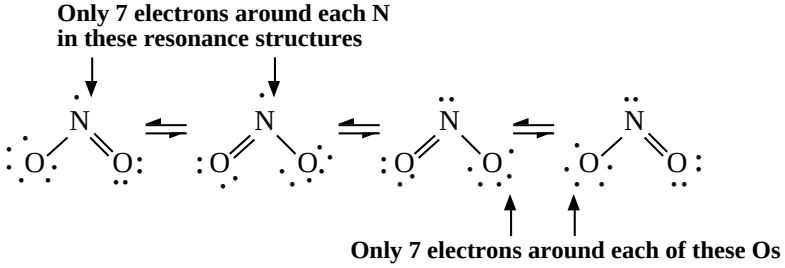
For some compounds and multi-atom ions it is possible to draw two or more equivalent arrangements of electrons. As an example consider the following for sulfur dioxide:



An atom of sulfur and 2 atoms of oxygen **compose a molecule of sulfur dioxide, SO_2, for which 2 equivalent electron structures may be drawn.**

It is seen that in order to have an octet of electrons around each atom, it is necessary to have a double bond between S and one of the Os. However, either O atom may be chosen, so that there are two equivalent structures, which are called **resonance structures**. Resonance structures are conventionally shown with a double arrow between them, as in the example above. They differ only in the locations of bonds and unshared electrons, not in the positions of the atoms. Although the name and structures might lead one to believe that the molecule shifts back and forth between the structures, this is not the case, and the molecule is a hybrid between the two.

Another compound with different resonance forms is nitrogen dioxide, NO_2:



Four resonance structures of NO_2.

This compound is produced in smog-forming atmospheres from pollutant NO emitted by automobile engines and is a major air pollutant. It is seen above that there

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are two aspects of the electron structure of NO_2 relating to material that is under discussion. First, there are 4 resonance structures. Second, in both of these resonance structures, there is 1 atom with an incomplete octet of outer shell electrons. This is because NO_2 has an uneven number of electrons. This type of compound is, therefore, an exception to the octet rule. The molecule has an "extra" electron for which there is no other electron to form an electron pair. Compounds consisting of molecules with such an electron are attracted by a magnetic field and are said to be **paramagnetic**.

4.7 CHEMICAL FORMULAS OF COMPOUNDS

What a Chemical Formula States

Chemical formulas were introduced in Chapter 1, and a number of them have been given so far, such as H_2O for water and CO_2 for carbon dioxide. In this and later sections, chemical formulas and their meaning are discussed in more detail. A chemical formula contains a lot of information. It is one of the most important tools for communicating in chemical language. Therefore, it is important to understand what a chemical formula means, and how to use it properly.

To best illustrate all of the information contained in a chemical formula, consider the moderately complicated example of calcium phosphate, $Ca_3(PO_4)_2$. This compound is composed of Ca^{2+} ions, each of which has a +2 charge, and phosphate ions, PO_4^{3-}, each with a -3 charge. The 4 oxygen atoms and the phosphorus atom in the phosphate ion are held together with covalent bonds. The calcium and phosphate ions are bonded together ionically in a lattice composed of these two kinds of ions. Therefore, both ionic and covalent bonds are involved in calcium phosphate. Figure 4.16 summarizes the information contained in the calcium phosphate formula.

Percentage Composition from Chemical Formulas

The percentage elemental composition of a chemical compound is readily calculated from either its empirical or molecular formula. One way to calculate the percentage composition of a compound is to consider a mole of the compound and

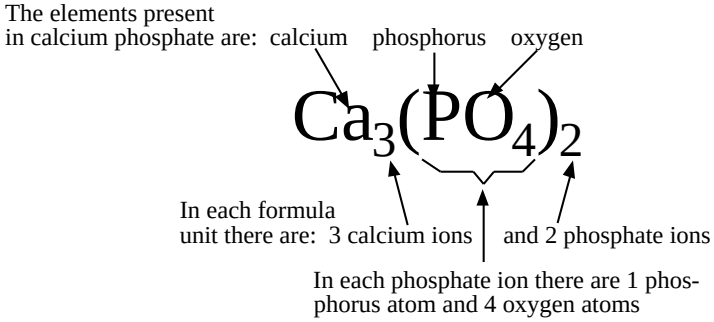


Figure 4.16 Summary of information contained in the chemical formula of calcium phosphate.

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Exercise: In the formula for aluminum sulfate, $A1_2(SO_4)_3$.

(a) the elements present are _____, _____, and _____.

(b) In each formula unit there are _____ $A1^{3+}$ ions and _____ SO_4^{2-} ions.

(c) Each sulfate ion contains _____ sulfur atoms and _____ oxygen atoms.

(d) The total number of each kind of atom in a formula unit of $A1_2(SO_4)_3$ is _____ A1, _____ S, and _____ O.

Answers: (a) aluminum, sulfur, and oxygen; (b) 2, 3; (c) 1, 4; (d) 2, 3, 12.

figure out the number of grams of each element in 1 mole of the compound, then calculate the percentages. This can be shown with glucose (blood sugar), molecular formula $C_6H_{12}O_6$. The subscripts indicate that each mole of glucose contains 6 mol C, 12 mol H, and 6 mol O. The mass of each element in a mole of glucose and the mass of a mole of glucose are given by the following:

For C: $6 \text{ mol} \times \frac{12.01 \text{ g}}{1 \text{ mol}} = 72.06 \text{ g}$

For H: $12 \text{ mol} \times \frac{1.01 \text{ g}}{1 \text{ mol}} = 12.12 \text{ g}$

For O: $6 \text{ mol} \times \frac{16.00 \text{ g}}{1 \text{ mol}} = 96.00 \text{ g}$

Molar mass of glucose = 180.18 g

The percentage of each element in glucose is given as follows:

Percent C: $\frac{72.06 \text{ g}}{180.18 \text{ g}} \times 100 = 40.0\%$

Percent H: $\frac{12.12 \text{ g}}{180.18 \text{ g}} \times 100 = 6.7\%$

Percent O: $\frac{96.0 \text{ g}}{180.18 \text{ g}} \times 100 = 53.3\%$

Example: What is the percentage elemental composition of calcium oxalate, CaC_2O_4?

Answer: Exactly 1 mole of CaC_2O_4 contains 1 mol Ca, 2 mol C and 4 mol O. Therefore,

For Ca: $1 \text{ mol} \times \frac{40.08 \text{ g}}{1 \text{ mol}} = 40.08 \text{ g}$ Percent Ca = $\frac{40.08 \text{ g}}{128.10 \text{ g}} \times 100 = 31.29\%$

For C: $2 \text{ mol} \times \frac{12.01 \text{ g}}{1 \text{ mol}} = 24.02 \text{ g}$ Percent Ca = $\frac{24.02 \text{ g}}{128.10 \text{ g}} \times 100 = 18.75\%$

For O: $4 \text{ mol} \times \frac{16.00 \text{ g}}{1 \text{ mol}} = 64.00 \text{ g}$ Percent Ca = $\frac{64.00 \text{ g}}{128.10 \text{ g}} \times 100 = 49.96\%$

Molar mass CaC_2O_4 = 128.10 g (per mol) Total = 100.0%

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Calculation of Chemical Formulas

In earlier sections of this chapter it was shown how the chemical formulas of some compounds follow logically from the sharing or exchange of electrons in accordance with the octet rule. However, long before the nature of atoms or the existence of electrons was known, accurate chemical formulas were written for many common compounds. In this section it is shown how chemical formulas are calculated from laboratory data.

First consider the calculation of the **empirical formula** of a chemical compound. The empirical formula gives the lowest whole number values of atoms in the formula. This may not be the same as the **molecular formulas** of substances that exist as molecules, which show the total number of each kind of atom in a molecule. For example, the empirical formula of benzene, one of the hydrocarbons with good engine performance properties in gasoline, is CH. However each molecule of benzene contains 6 C atoms and 6 H atoms, so the molecular formula is C_6H_6, illustrating the true number of each of the two kinds of atoms in the molecule.

Before calculating some empirical formulas, it is important to know what is meant by a mole of substance. The mole concept was discussed in detail in Section 2.3 and is summarized below:

1. The mole is based upon the number of particles or entities in a substance. These may be molecules of an element or compound, atoms of an element, atoms of a specified element in a particular mass of a compound, or ions in a compound.
2. In expressing moles, it is essential to state clearly the entity being described, such as atoms of Si, molecules of F_2, molecules of H_2O, formula units (see Section 2.3) of ionic Na_2SO_4, or ions of Na^+.
3. A mole of an entity contains Avogadro's number, 6.02×10^{23}, of that entity.
4. The mass of a mole (molar mass) of an element, compound, or portion of a compound (such as the SO_4^{2-} ion in Na_2SO_4) is the mass in grams equal numerically to the atomic mass, molecular mass, or formula mass. For example, given 23.0, 32.1, and 16.0 for the atomic masses of Na, S, and O, respectively, the following can be stated: (a) A mole of Na atoms has a mass of 23.0 g, (b) a mole of Na_2SO_4 has a mass of $2 \times 23.0 + 32.1 + 4 \times 16.0 = 142.1$ g, and (c) a mole of SO_4^{2-} ions has a mass of $32.1 + 4 \times 16.0 = 96.1$ g.
5. Number of moles of substance =

$$\frac{\text{mass of substance in grams}}{\text{molar mass of substance in grams per mole}} \qquad (4.7.1)$$

Empirical Formula from Percentage Composition

Suppose that the only two elements in a compound are phosphorus and oxygen and that it is 43.64% P and 56.36% O by mass. The following steps can be used to find the empirical formula of the compound:

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1. From the percentages, it follows that for each 100 grams of compound there are 43.64 g of P and 56.36 g of O. The number of moles of each of these elements in exactly 100 g of the compound is calculated from the number of grams of each per mole of compound as follows:

$$43.64 \text{ g compound} \times \frac{1 \text{ mol P}}{30.97 \text{ g P}} = 1.409 \text{ mol P} \qquad (4.7.2)$$

↑	↑	↑
In 100.0 g of the compound there are 43.64 g of P	In 1 mol of P there are 30.97 g of P (from the atomic mass of P)	Therefore, 100.0 g of the compound contains 1.409 mol of P

$$56.36 \text{ g compound} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 3.523 \text{ mol O} \qquad (4.7.3)$$

↑	↑	↑
In 100.0 g of the compound there are 56.36 g of O	In 1 mol of O there are 16.00 g of O (from the atomic mass of O)	Therefore, 100.0 g of the compound contains 3.523 mol of O

2. Calculate the relative number of moles of O per mole of P.

$$\frac{3.523 \text{ mol O}}{1.409 \text{ mol P}} = \frac{2.500 \text{ mol O}}{1.000 \text{ mol P}} \qquad (4.7.4)$$

3. Calculate the ratio of moles of O to moles of P in terms of whole numbers. The denominator of the ratio, 2.500 mol O/1.000 mol P is already a whole number, and the numerator can be converted to a whole number (5) if it is multiplied by 2. Therefore, both the numerator and the denominator are multiplied by 2 to get the whole number ratio,

$$\frac{2.500 \text{ mol O}}{1.000 \text{ mol P}} \times \frac{2}{2} = \frac{5.000 \text{ mol O}}{2.000 \text{ mol P}} \qquad (4.7.5)$$

4. Knowing the ratio of moles, write the empirical formula of the compound.

$$P_2O_5$$

The empirical formula does not necessarily give the actual number of atoms per molecule; it gives the smallest whole number ratio for the number of each kind of atom in the molecule. The molecular formula of this compound is P_4O_{10}, indicating that a molecule of it contains twice the number of each kind of atom indicated by the empirical formula. The correct name of the compound is tetraphosphorus decoxide. It is made commercially by burning elemental phosphorus in dry air. It reacts violently with water to produce commercially important orthophosphoric acid, H_3PO_4. The strong affinity of P_4O_{10} for water makes P_4O_{10} very useful as a drying and dehydrating agent.

Empirical formulas are actually determined in the laboratory by chemical analyses for each element in the compound. There is always some error involved in such an analysis, so the numbers obtained for the ratios of one element to another

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may not be as nicely rounded as in the example of the calculation of the empirical formula P_2O_5. As an example of this, consider that a compound used as an inert filler in laundry detergent was found by chemical analysis to be 32.59% Na, 22.74% S, and 44.67% O. What is the empirical formula of the compound?

1. According to the percentages given, there are 32.59 g of Na, 22.74 g of S and 44.67 g of O in 100.0 g of the compound. Using the appropriate atomic masses gives the following number of moles of each element in 100 g of the compound:

$$32.59 \text{ g Na} \times \frac{1 \text{ mol Na}}{22.99 \text{ g Na}} = 1.418 \text{ mol Na} \tag{4.7.6}$$

$$22.74 \text{ g S} \times \frac{1 \text{ mol S}}{32.06 \text{ g S}} = 0.7093 \text{ mol S} \tag{4.7.7}$$

$$44.67 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.792 \text{ mol O} \tag{4.7.8}$$

2. Of the three elements present, the element with the least number of moles is sulfur. Therefore, the ratios of the number of moles of each of the other elements relative to a mole of S is calculated.

$$\frac{1.418 \text{ mol Na}}{0.7093 \text{ mol S}} = \frac{1.999 \text{ mol Na}}{1.000 \text{ mol S}} \tag{4.7.9}$$

$$\frac{2.792 \text{ mol O}}{0.7093 \text{ mol S}} = \frac{3.936 \text{ mol O}}{1.000 \text{ mol S}} \tag{4.7.10}$$

3. Examination of the results above shows that, rounding 1.999 to 2 and 3.936 to 4, there are 2 moles of Na and 4 moles of O per mole of S, leading to the empirical formula,

$$Na_2SO_4$$

This compound is called sodium sulfate.

Example: Analysis of a compound shows it to be 26.49% potassium, 35.58% Cr, and 37.93% O. What is the empirical formula of the compound?

Answer: In 100.0 g of the compound there are 26.49 g K, 35.58 g Cr, and 37.93 g O, and the following number of moles of each element:

$$26.49 \text{ g K} \times \frac{1 \text{ mol K}}{39.10 \text{ g K}} = 0.6775 \text{ mol K} \tag{4.7.11}$$

$$35.58 \text{ g Cr} \times \frac{1 \text{ mol Cr}}{52.00 \text{ g Cr}} = 0.6842 \text{ mol Cr} \tag{4.7.12}$$

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$$37.93 \text{ g O} \times \frac{1 \text{ mol O}}{16.00 \text{ g O}} = 2.371 \text{ mol O} \quad (4.7.13)$$

Examination of the above figures reveals that there is essentially the same number of moles of K and Cr in a gram of the compound (rounding gives 0.68 mole of each per gram of compound), whereas there is a higher number of moles of O. Calculating the number of moles of K and O relative to the number of moles of Cr gives the following:

$$\frac{0.6775 \text{ mol K}}{0.6842 \text{ mol Cr}} \times 100.0 \text{ g compound} = 0.9902 \text{ mol K} \quad (4.7.14)$$

$$\frac{2.371 \text{ mol O}}{0.6842 \text{ mol Cr}} \times 100.0 \text{ g compound} = 3.465 \text{ mol O} \quad (4.7.15)$$

Rounding these numbers to the nearest 0.1 mol gives 1.0 mol of K and 3.5 mol of O per mol of Cr. One can write the empirical formula as,

$$KCrO_{3.5}$$

but this does not give a whole number of O atoms in the formula unit. Multiplying the subscripts by 2 (in the formula above there is understood to be a subscript 1 after K and after Cr) yields an empirical formula with whole numbers of atoms:

$$K_2Cr_2O_7$$

This is the formula of the compound potassium dichromate, each formula unit of which consists of 2 K^+ ions and a dichromate ion, $Cr_2O_7^{2-}$.

4.8 THE NAMES OF CHEMICAL COMPOUNDS

One of the more important aspects of chemical language is the correct use of names for chemical compounds—chemical nomenclature. So far in the text the names of a number of compounds have been given. This section presents a systematic approach to the naming of inorganic compounds. These are all of the compounds that do not contain carbon plus a few—such as CO_2 and Na_2CO_3—that do contain carbon. Most carbon-containing compounds are organic compounds; organic compound nomenclature will not be considered here; it is discussed in Chapter 10. Inorganic nomenclature will be divided into several categories so that it can be approached in a systematic manner.

Binary Molecular Compounds

In this section the rules for naming binary molecular compounds—those composed of only two elements bonded together as molecules—are examined. Most such compounds are composed of nonmetallic elements. In a binary molecular com-

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pound, one of the elements is usually regarded as being somewhat more positive than the other. This is a result of unequal sharing of electrons in covalent bonds, a characteristic of bonds considered briefly in Section 4.6. The symbol of the element with a more positive nature is given first in the chemical formula of a binary compound. For example, in HCl, hydrogen is regarded as having a somewhat more positive, and Cl a somewhat more negative, character.

In naming binary molecular compounds, the first part of the name is simply that of the first element in the chemical formula, and the second part of the name is that of the second element with an *-ide* ending. Therefore, the name of HCl is hydrogen chloride. In most cases, however, it is necessary to have prefixes to designate the relative number of atoms in the molecular formula. These prefixes are the following:

1-mono	3-tri	5-penta	7-hepta	9-nona
2-di	4-tetra	6-hexa	8-octa	10-deca

The uses of these prefixes are illustrated by the names of several oxygen compounds (oxides) in Table 4.2. Other examples of compounds in which prefixes are used for naming are $SiCl_4$, silicon tetrachloride; Si_2F_6, disilicon hexafluoride; PCl_5, phosphorus pentachloride; and SCl_2, sulfur dichloride.

It is seen from the examples given that the prefix is omitted before the name of the first element in the chemical formula when there is only 1 atom of that element per molecule. In cases where the name of the second element in a binary molecular compound formula begins with a vowel, the "a" or "o" at the end of the prefix may be deleted. Thus, CO is called carbon monoxide, rather than carbon monooxide and Cl_2O_7 is called dichlorine heptoxide, not dichlorine heptaoxide.

A number of compounds, including those other than binary molecular compounds, have been known for so long and have been so widely used that they have acquired common names that do not describe their chemical formulas. The best example of these is H_2O, which is always known as water, not dihydrogen monoxide. Other examples are H_2O_2, hydrogen peroxide; NH_3, ammonia; and N_2O, nitrous oxide.

Table 4.2 Some Oxides and Their Names

Formula	Name	Formula	Name
CO	Carbon monoxide	SO_2	Sulfur dioxide
CO_2	Carbon dioxide	SO_3	Sulfur trioxide
N_2O_5	Dinitrogen pentoxide	SiO_2	Silicon dioxide
N_2O_4	Dinitrogen tetroxide	P_2O_4	Diphosphorus tetroxide
NO_2	Nitrogen dioxide	P_4O_7	Tetraphosphorus heptoxide
NO	Nitrogen monoxide	P_4O_{10}	Tetraphosphorus decoxide
N_2O	Dinitrogen oxide (nitrous oxide)	Cl_2O_7	Dichlorine heptoxide

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Names of Ionic Compounds

Recall that ionic compounds consist of aggregates of positively charged cations and negatively charged anions held together by the mutual attraction of their opposite electrical charges. The easiest of these compounds to visualize are those that are composed of only two elements, the cation formed by the loss of all its outer shell electrons and the anion formed by the gain of enough outer shell electrons to give it a stable octet of outer electrons (as shown for sodium and chlorine in Equation 4.3.1). The formation of such ions is readily shown by consideration of some of the elements in the abbreviated version of the periodic table in Figure 4.2, as illustrated by the following half-reactions (literally "half a reaction" in which electrons are reactants or products):

Half-reactions for cation formation

$$Li\cdot \longrightarrow Li^{+} + e^{-} \qquad Mg: \longrightarrow :Mg:^{2+} + 2e^{-}$$

$$Na\cdot \longrightarrow :Na:^{+} + e^{-} \qquad Ca: \longrightarrow :Ca:^{2+} + 2e^{-}$$

$$K\cdot \longrightarrow :K:^{+} + e^{-} \qquad Al: \longrightarrow :Al:^{3+} + 3e^{-}$$

Half-reactions for anion formation

$$\cdot N: + 3e^{-} \longrightarrow :N:^{3-} \qquad H\cdot + e^{-} \longrightarrow H:^{-}$$

$$\cdot O: + 2e^{-} \longrightarrow :O:^{2-} \qquad \cdot F: + e^{-} \longrightarrow :F:^{-}$$

$$\cdot S: + 2e^{-} \longrightarrow :S:^{2-} \qquad \cdot Cl: + e^{-} \longrightarrow :Cl:^{-}$$

The cations formed as shown by the half-reactions above are simply given the names of the metals that produced them, such as sodium for Na^{+} and calcium for Ca^{2+}. Since they consist of only one element, the name for each anion has an -ide ending, that is, N^{3-}, nitride; O^{2-}, oxide; S^{2-}, sulfide; H^{-}, hydride; F^{-}, fluoride; and Cl^{-}, chloride. An advantage in the nomenclature of ionic compounds is that it is not usually necessary to use prefixes to specify the numbers of each kind of ion in a formula unit. This is because the charges on the ions determine the relative numbers of each as shown by the examples in Table 4.3.

Exercise: For the compounds listed below, where x and y are unspecified subscripts, give the compound formula and name.

(a) K_xCl_y	(d) Li_xCl_y	(g) K_xN_y	(j) Mg_xO_y
(b) K_xS_y	(e) Li_xF_y	(h) Ca_xN_y	(k) Ca_xO_y
(c) Al_xF_y	(f) Li_xO_y	(i) Mg_xN_y	(l) Ca_xS_y

Answers: (a) KCl, potassium chloride; (b) K_2S, potassium sulfide; (c) AlF_3, aluminum fluoride; (d) LiCl, lithium chloride; (e) LiF, lithium fluoride; (f) Li_2O,

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lithium oxide, (g) K_3N, potassium nitride; (h) Ca_3N_2, calcium nitride; (i) Mg_3N_2, magnesium nitride; (j) MgO, magnesium oxide; (k) CaO, calcium oxide; (l) CaS, calcium sulfide.

Table 4.3 Formulas and Names of Ionic Compounds Formed from Two Elements

Ionic compound formula	Compound name	Neutral compound formed from the ions below
NaF	Sodium fluoride	One +1 ion and one -1 ion
K_2O	Potassium oxide	Two +1 ions and one -2 ion
Na_3N	Sodium nitride	Three +1 ions and one -3 ion
$MgCl_2$	Magnesium chloride	One +2 ion and two -1 ions
CaH_2	Calcium hydride	One +2 ion and two -1 ions
$AlCl_3$	Aluminum chloride	One +3 ion and three -1 ions
Al_2O_3	Aluminum oxide	Two +3 ions and three -2 ions

4.9 ACIDS, BASES, AND SALTS

Most inorganic chemical compounds belong to one of three classes — acids, bases, or salts. These three categories of compounds are addressed briefly in this section and in more detail in Chapter 6.

Acids

For the present an acid can be defined as a substance that dissolves in water to produce hydrogen ion, $H^+(aq)$. (Recall that *aq* in parentheses after a species formula shows that it is dissolved in water.) The most obviously acidic compounds are those that contain ionizable H in their formulas. Typically, hydrogen chloride gas, HCl(*g*), dissolves in water,

$$HCl(g) \xrightarrow{H_2O} H^+(aq) + Cl^-(aq) \qquad (4.9.1)$$

and completely dissociates (falls apart) to give an aqueous solution containing H^+ cation and Cl^- anion. Note that the H_2O above the arrow in this chemical equation shows the reaction occurs in water. The presence of a substantial concentration of H^+ ions in water provides an acidic solution, in this case a solution of hydrochloric acid.

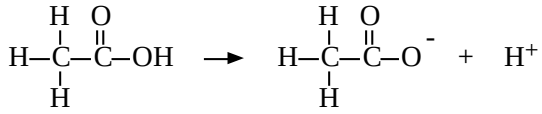
Some acids produce more than 1 hydrogen ion per molecule of acid. For example, sulfuric acid dissociates in two steps,

$$\underset{\text{Sulfuric acid}}{H_2SO_4(aq)} \rightarrow H^+(aq) + \underset{\text{hydrogen sulfate ion}}{HSO_4^-(aq)} \qquad (4.9.2)$$

$$HSO_4^-(aq) \rightarrow H^+(aq) + SO_4^{2-}(aq) \qquad (4.9.3)$$

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to yield 2 H^+ per H_2SO_4 molecule; the second of the 2 hydrogen ions comes off much less readily than the first. Some acids have hydrogen atoms that do not produce H^+ ion in water. For example, each molecule of acetic acid produces only one H^+ ion when it dissociates in water; the other 3 H atoms stay covalently bonded to the acetate ion:



(4.9.4)

Some of the most widely produced industrial chemicals are acids. Sulfuric acid ranks first among all chemicals produced in the United States with production of almost 40 million metric tons per year. Its greatest single use is in the production of phosphate fertilizers, and it has applications in many other areas including petroleum refining, alcohol synthesis, iron and steel pickling (corrosion removal), and storage battery manufacture. Nitric acid ranks about 10th among U.S. chemicals with annual production of 7–8 million metric tons, and hydrochloric acid is about 25th at about 3 million metric tons (annual production and rank vary from year to year).

The naming of acids is addressed in more detail in Chapter 6. Briefly, acids that contain only H and another atom are "hydro-ic" acids, such as hydrochloric acid, HCl. For acids that contain two different amounts of oxygen in the anion part, the one with more oxygen is an "-ic" acid and the one with less is an "-ous" acid. This is illustrated by nitric acid, HNO_3, and nitrous acid, HNO_2. An even greater amount of oxygen is denoted by a "per-" prefix and less by the "hypo-ous" name. The guidelines discussed above are illustrated for acids formed by chlorine ranging from 0 to 4 oxygen atoms per acid molecule as follows: HCl, hydrochloric acid; HClO, hypochlorous acid; $HClO_2$, chlorous acid; $HClO_3$, chloric acid; $HClO_4$, perchloric acid.

Bases

A **base** is a substance that contains hydroxide ion OH^-, or produces it when dissolved in water. Most of the best known inorganic bases have a formula unit composed of a metal cation and 1 or more hydroxide ions. Typical of these are sodium hydroxide, NaOH, and calcium hydroxide, $Ca(OH)_2$, which dissolve in water to yield hydroxide ion and their respective metal ions. Other bases such as ammonia, NH_3, do not contain hydroxide ion, but react with water,

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad (4.9.5)$$

to produce hydroxide ion (this reaction proceeds only to a limited extent; most of the NH_3 is in solution as the NH_3 molecule).

Bases are named for the cation in them plus "hydroxide." Therefore, KOH is potassium hydroxide.

Salts

A **salt** is an ionic compound consisting of a cation other than H^+ and an anion other than OH^-. A salt is produced by a chemical reaction between an acid and a

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base. The other product of such a reaction is always water. Typical salt-producing reactions are given below:

$$\underset{\text{base}}{KOH} + \underset{\text{acid}}{HCl} \rightarrow \underset{\text{a salt, potassium chloride}}{KCl} + \underset{\text{water}}{H_2O} \quad (4.9.6)$$

$$\underset{\text{base}}{Ca(OH)_2} + \underset{\text{acid}}{H_2SO_4} \rightarrow \underset{\text{a salt, calcium sulfate}}{CaSO_4} + \underset{\text{water}}{2H_2O} \quad (4.9.7)$$

Except for those compounds in which the cation is H^+ (acids) or the anion is OH^- (bases), the compounds that consist of a cation and an anion are salts. Therefore, the rules of nomenclature discussed for ionic compounds in Section 4.8 are those of salts. The salt product of Reaction 4.9.6, above, consists of K^+ cation and Cl^- anion, so the salt is called potassium chloride. The salt product of Reaction 4.9.7, above, is made up of Ca^{2+} cation and SO_4^{2-} anion and is called calcium sulfate. The reaction product of LiOH base with H_2SO_4 acid is composed of Li^+ ions and SO_4^{2-} ions. It takes 2 singly charged Li^+ ions to compensate for the 2- charge of the SO_4^{2-} anion, so the formula of the salt is Li_2SO_4. It is called simply lithium sulfate. It is not necessary to call it dilithium sulfate because the charges on the ions denote the relative numbers of ions in the formula.

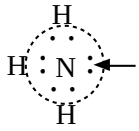
CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Chemical bonds are normally formed by the transfer or sharing of [1]_____ _____, which are those in the [2]_____. An especially stable group of electrons attained by many atoms in chemical compounds is an [3]_____. An ion consists of [4]_____ _____ _____. A cation has [5]_____ and an anion has [6]_____. An ionic compound is one that contains [7]_____ _____ and is held together by [8]_____. Both F^- and Mg^{2+} have the electron configuration [9]_____ identical to that of the neutral atom [10]_____. In visualizing a neutral metal atom reacting with a neutral nonmetal atom to produce an ionic compound, the three major energy factors are [11]_____ _____. The energy required to separate all of the ions in a crystalline ionic compound and remove them a sufficient distance from each other so that there is no interaction between them is called the [12]_____ _____. The ion formed from Ca is [13] _____, the ion formed from Cl is [14]_____, and the formula of the compound formed from these ions is [15]_____. A covalent bond may be described as [16] _____

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_____. In the figure,



each pair of dots between N and H represents [17]_____
_____ the arrow points to [18]_____
_____ and the circle outlines [19]_____
_____. A central atom refers to [20]_____

_____. A triple bond consists of [21]_____
and is represented in a structural chemical formula as [22]_____.
With increasing bond order (single<double<triple), bond length [23]_____ and bond strength [24]_____. Electronegativity refers to [25]_____
_____. A polar covalent bond is one in which [26]_____
_____. A coordinate covalent bond is [27]_____

_____. Three major exceptions to the octet rule are [28]_____

_____.
Resonance structures are those for which [29]_____
_____.
Chemical formulas consist of [30]_____

that tell the following about a compound [31]_____

_____. The percentage elemental composition of a chemical compound is calculated by [32] _____

_____. The empirical formula of a chemical compound is calculated by computing the masses of each consituent element in [33]_____
_____,
dividing each of the resulting values by [34]_____
_____, dividing each value by [35]_____,
and rounding to [36]_____.
The prefixes for numbers 1-10 used to denote relative numbers of atoms of each kind of atom in a chemical formula are [37]_____
_____.

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The compound N_2O_5 is called [38]_____. The ionic compound $AlCl_3$ is called [39]_____, which does not contain a "tri-" because [40]_____ _____. Ammonium ion, NH_4^+, is classified as a [41]_____ meaning that it consists of [42]_____ _____. An acid is [43]_____ _____. A base is [44]_____ _____. A salt is [45]_____ _____ and is produced by [46]_____. The other product of such a reaction is always [47]_____.

Answers to Chapter Summary

1. valence electrons
2. outermost shell of the atom
3. octet of outer electrons
4. an atom or group of atoms having an unequal number of electrons and protons and, therefore, a net electrical charge
5. a positive charge
6. a negative charge
7. cations and anions
8. ionic bonds
9. $1s^2 2s^2 2p^6$
10. neon
11. ionization energy, electron affinity, and lattice energy
12. lattice energy
13. Ca^{2+}
14. Cl^-
15. $CaCl_2$
16. one that joins 2 atoms through the sharing of 1 or more pairs of electrons between them
17. a pair of electrons shared in a covalent bond
18. an unshared pair of electrons
19. a stable octet of electrons around the N atom
20. an atom to which several other atoms are bonded
21. 3 pair (total of 6) electrons shared in a covalent bond
22. ≡ or ⁚⁚
23. decreases
24. increases
25. the ability of a bonded atom to attract electrons to itself
26. the electrons involved are not shared equally
27. one in which only 1 of the 2 atoms contributes the two electrons in the bond

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28. molecules with an uneven number of valence electrons, molecules in which an atom capable of forming an octet has fewer than 8 outer electrons, and molecules in which an atom has more than 8 outer electrons
29. it is possible to draw two or more equivalent arrangements of electrons
30. atomic symbols, subscripts, and sometimes parentheses and charges
31. elements in it, relative numbers of each kind of atom, charge, if an ion
32. dividing the mass of a mole of a compound into the mass of each of the constituent elements in a mole
33. 100 g of the element
34. the atomic mass of the element
35. the smallest value
36. the smallest whole number for each element
37. 1-mono, 2-di,3-tri, 4-tetra, 5-penta, 6-hexa, 7-hepta, 8-octa, 9-nona, 10-deca
38. dinitrogen pentoxide
39. aluminum chloride
40. the charges on ions are used to deduce chemical formulas
41. polyatomic ion
42. 2 or more atoms per ion
43. a substance that dissolves in water to produce hydrogen ion, $H^+(aq)$
44. a substance that contains hydroxide ion OH^-, or produces it when dissolved in water
45. an ionic compound consisting of a cation other than H^+ and an anion other than OH^-.
46. a chemical reaction between an acid and a base
47. water

QUESTIONS AND PROBLEMS

Section 4.1. Chemical Bonds and Compound Formation

1. Chlorofluorocarbons (Freons) are composed of molecules in which Cl and F atoms are bonded to 1 or 2 C atoms. These compounds do not break down well in the atmosphere until they drift high into the stratosphere, where very short wavelength ultraviolet electromagnetic radiation from the sun is present, leading to the production of free Cl atoms that react to deplete the stratospheric ozone layer. Recalling what has been covered so far about the energy of electromagnetic radiation as a function of wavelength, what does this say about the strength of C-Cl and C-F bonds?

Section 4.2. Chemical Bonding and the Octet Rule

2. Illustrate the octet rule with examples of (a) a cation, (b) an anion, (c) a diatomic elemental gas, and (d) a covalently bound chemical compound.

Section 4.3. Ionic Bonding

3. When elements with atomic numbers 6 through 9 are covalently or ionically bound, or when Na, Mg, or A1 have formed ions, which single element do their

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outer electron configurations most closely resemble? Explain your answer in terms of filled orbitals.

4. Ionic bonds exist because of (a)_____between (b) _____ _____.

5. In the crystal structure of NaCl, what are the number and type of ions that are nearest neighbors to each Na^+ ion?

6. What major aspect of ions in crystals is not shown in Figure 4.5?

7. What are five energy factors that should be considered in the formation of ionic NaCl from solid Na and gaseous Cl_2?

8. What are two major factors that increase the lattice energy of ions in an ionic compound?

9. Is energy released or is it absorbed when gaseous ions come together to form an ionic crystal?

10. What is incomplete about the statement that "the energy change from lattice energy for NaCl is 785 kilojoules of energy released?

11. How do the sizes of anions and cations compare with their parent atoms?

12. How do the sizes of monatomic (one-atom) cations and anions compare in the same period?

Section 4.4. Fundamentals of Covalent Bonding

13. Define covalent bond.

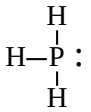
14. Explain the energy minimum in the diagram illustrating the H-H covalent bond in Figure 4.9.

Section 4.5. Covalent Bonds in Compounds

15. What may be said about the liklihood of H atoms being involved in double covalent bonds?

16. What is represented by a dashed line, –, in a chemical formula?

17. What is represented by the two dots in the formula of phosphine, PH_3, below:



Section 4.6. Some other Aspects of Covalent Bonding

18. What are multiple bonds? Which three elements are most likely to form multiple bonds?

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19. What can be said about the nature of covalent bonds between (a) 2 atoms with almost identical electronegativity values and (b) 2 atoms with substantially different electronegativity values?

20. What symbols are used to show bond polarity?

21. What is the "ultimate" in polar bonds?

22. A molecule of NH_3 will combine with one of BF_3. Describe the kind of bond formed in the resulting compound.

23. What is required for an atom to form a compound with more than 8 electrons in the central atom's outer shell?

24. What are resonance structures?

25. How many total valence electrons are in the nitrate ion, NO_3^-? What are the resonance structures of this ion?

Section 4.7. Chemical Formulas of Compounds

26. Summarize the steps involved in calculating the percentage composition of a compound from its formula.

27. Phosgene, $COCl_2$, is a poisonous gas that was used for warfare in World War I. What is its percentage composition?

28. The molecular formula of acetylsalicylic acid (aspirin) is $C_9H_8O_4$. What is its percentage composition?

29. Hydrates are compounds in which each formula unit is associated with a definite number of water molecules. A typical hydrate is copper (II) sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$. The water of hydration can be driven off by heating, leaving the anhydrous compound. Answer the following pertaining to $CuSO_4 \cdot 5H_2O$: (a) Mass of 1 mole of the compound, (b) mass of H_2O in 1 mole of $CuSO_4 \cdot 5H_2O$, (c) percentage of H_2O in $CuSO_4 \cdot 5H_2O$.

30. What are the percentages of oxygen in (a) perchloric acid, (b) chloric acid, (c) chlorous acid, and (d) hypochlorous acid (these acids were discussed in this chapter).

31. What is the simplest (empirical) formula of sodium oxalate, $Na_2C_2O_4$?

32. What is the formula of dichlorine heptoxide? What is its percentage composition?

33. Chlorine dioxide, ClO_2, is used as a substitute for chlorine gas in the disinfection of drinking water. What is the percentage composition of ClO_2?

34. Summarize in steps the calculation of empirical formula from the percentage composition of a compound.

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35. If the empirical formula and the actual formula mass (molecular mass) of a compound are known, how is the true formula calculated?

36. A chlorofluorocarbon gas is 9.93% C, 31.43% F, and 58.64% Cl. What is its empirical formula?

37. A 100.0 g portion of the chlorofluorocarbon gas (preceding question) was found to occupy 25.3 L at 100°C and 1.000 atm pressure. Assuming that the gas behaved ideally and using the ideal gas equation, how many moles of the gas are in 100.0 of Freon? What is its molar mass? What is its molecular formula? (To answer this question it may be necessary to refer back to a discussion of the gas laws in Section 2.6).

38. A compound is 5.88% H and 94.12% O. What is its empirical formula?

39. The compound from the preceding problem has a molecular mass of 34.0. What is its molecular formula?

40. A pure liquid compound with an overpowering vinegar odor is 40.0% C, 6.67% H, and 53.3% O. Its molecular mass is 60.0. What is its empirical formula? What is its molecular formula?

41. A compound is 29.1% Na, 40.5% S, and 30.4% O. It has a formula mass of 158.0. Fill out the table below pertaining to the compound, give its true formula, and give its actual formula. It is an ionic compound. What is the anion?

Element	Grams of element in 100 g compound	Mol element in 100 g compound	Mol element / mol element with fewest moles
Na	(a) _____	(d) _____	(g) _____
S	(b) _____	(e) _____	(h) _____
O	(c) _____	(f) _____	(i) _____

42. An ionic compound is 41.7% Mg, 54.9% O, and 3.4% H. What is its empirical formula? Considering the ions in Table 3.6, what is the actual formula?

43. Ethylenediamine is 40.0% C, 13.4% H, and 46.6% N; its formula mass is 60.1. What are its empirical and molecular formulas?

44. The empirical formula of butane is C_2H_5 and its molecular mass is 58.14. What is the molecular formula?

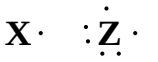
General Questions

45. Suppose that you were asked to give the Lewis formula of formic acid, H_2CO_2, where the atomic number of H is 1, that of C is 6, and that of O is 8. The total number of valence (outer shell) electrons that would have to be placed correctly in the structure is

 A. 6 C. 20 E. 16 B. 18 D. 7

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46. Given the Lewis symbols of hypothetical elements X and Z,



The compound most likely formed by these two elements would be

A. Covalently bound compound formula X_2Z_3.
B. Covalently bound compound formula XZ.
C. Ionic compound formula X_2Z.
D. Ionic compound XZ_2.
E. Ionic compound XZ.

47. Of the following, the statement that is **untrue** regarding ionic NaCl and its formation from gaseous Na and Cl atoms is

A. Energy called electron repulsion is consumed in putting an electron on a Cl atom to produce a Cl^- ion.
B. Energy called ionization energy is required to remove an electron from a Na atom to produce a Na^+ ion.
C. A relatively large amount of energy (lattice energy) is released when the Na^+ and Cl^- ions come together to form crystalline NaCl.
D. A particular Cl^- ion in the crystal of NaCl has 6 Na^+ ions as its nearest neighbors.
E. Every ion in the crystal of NaCl is closest to ions of opposite charge, resulting in forces of attraction that account for the stability of ionic bonds.

48. Consider the single, double, and triple bonds connecting the 2 carbon atoms in the 3 compounds C_2H_6, C_2H_4, and C_2H_2. Of the following pertaining to these bonds, the **untrue** statement is

A. The C=C bond is shorter than the C–C bond.
B. The C≡C bond is stronger than the C=C bond.
C. Because it must accomodate a total of 6 electrons rather than 2, the C≡C bond is longer than the C–C bond.
D. As bond multiplicity increases, the bond strength increases and the bond length decreases.
E. The bonds can act like springs in that the atoms connected by the bonds vibrate when exposed to the right wavelength of infrared radiation.

49. Remember that O and S atoms all have the same number of valence electrons. Considering the structures (Lewis formulas),



the true statement is

A. Only one of these structures can be correct.
B. Both of these structures are incorrect.
C. The structure on the left shows the incorrect number of outer shell electrons for the O atom on the left.
D. The structures are equivalent resonance structures.
E. The text showed the sulfur atom on one end, not in the middle.

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Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

5 CHEMICAL REACTIONS, EQUATIONS, AND STOICHIOMETRY

5.1 THE SENTENCES OF CHEMISTRY

As noted earlier, chemistry is a language. Success in the study of chemistry depends upon how well chemical language is learned. This chapter presents the last of the most basic parts of the chemical language. When it has been learned, the reader will have the essential tools needed to speak and write chemistry and to apply it in environmental and other areas.

Recall that the discussion of chemical language began by learning about the *elements*, the *atoms* composing the elements, and the *symbols* used to designate these elements and their atoms. Atoms of the elements bond together in various combinations to produce *chemical compounds*. These are designated by *chemical formulas* consisting of symbols for the kinds of atoms in the compound and subscripts indicating the relative numbers of atoms of each kind in the compound. In chemical language, the symbols of the elements are the letters of the chemical alphabet and the formulas are the words of chemistry.

Chemical Reactions and Equations: The Sentences of the Chemical Language

The formation of chemical compounds, their decomposition, and their interactions with one another fall under the category of **chemical reactions**. Chemical reactions are involved in the annual production of millions of kilograms of industrial chemicals, bacterially mediated degradation of water pollutants, the chemical analysis of the kinds and quantities of components of a sample, and practically any other operation involving chemicals. To a very large extent, chemistry is the study of chemical reactions expressed on paper as chemical equations. A **chemical equation** is a sentence of chemistry, made up of words consisting of chemical formulas. A sentence should be put together according to rules understood by all those literate in the language. The rules of the chemical

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language are particularly rigorous. Although a grammatically sloppy sentence in a spoken language can still convey a meaningful message, a chemical equation with even a small error is misleading and often meaningless.

Quantitative Calculations from Chemical Equations

Chemistry is a quantitative science, and it is important to know how to do some of the basic chemical calculations early in a beginning chemistry course. Among the most important of these are the calculations of the quantities of substances consumed or produced in a chemical reaction. Such calculations are classified as **stoichiometry**. Heat is normally evolved or taken up in the course of a chemical reaction. The calculation of the quantity of heat involved in a reaction falls in the branch of chemistry called **thermochemistry**.

5.2 THE INFORMATION IN A CHEMICAL EQUATION

Chemical Reactions

A chemical reaction is a process involving the breaking and/or formation of chemical bonds and a change in the chemical composition of the materials participating in the reaction. A chemical reaction might involve the combination of two elements to form a compound. An example of this is the reaction of elemental hydrogen and oxygen to produce the compound water. Passage of an electrical current through water can cause the compound to break down and produce elemental hydrogen and oxygen. When wood burns, cellulose, a compound in the wood, reacts with elemental oxygen in air to produce the two compounds, carbon dioxide and water. If the carbon dioxide produced is bubbled through a solution of the compound calcium hydroxide dissolved in water, it produces the compounds calcium carbonate (a form of limestone) and water. Energy is involved in chemical reactions; some reactions produce energy, others require it in order for them to occur.

Expressing a Chemical Reaction as a Chemical Equation

A **chemical equation** is a means of expressing what happens when a chemical reaction occurs. It tells what reacts, what is produced, and the relative quantities of each. The information provided can best be understood by examining a typical chemical equation. For example, consider the burning of propane, a gas extracted from petroleum that is widely used for heating, cooking, grain drying, and other applications in which a clean-burning fuel is needed in areas where piped natural gas is not available. When propane burns in a camp stove, it reacts with oxygen in the air. The chemical equation for this reaction and the information in it are the following:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad (5.2.1)$$

- Propane reacts with oxygen to give carbon dioxide and water.

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- There are two reactants on the left side of the equation—propane, chemical formula C_3H_8, and oxygen, chemical formula O_2.
- There are two products on the right side of the equation—carbon dioxide, chemical formula CO_2, and water, chemical formula H_2O.
- For the smallest possible unit of this reaction, 1 propane molecule reacts with 5 oxygen molecules to produce 3 carbon dioxide molecules, and 4 water molecules, as shown by the respective numbers preceding the chemical formulas (there is understood to be a 1 in front of the C_3H_8).
- There are 3 C atoms altogether on the left side of the equation, all contained in the C_3H_8 molecule, and 3 C atoms on the right side contained in 3 molecules of CO_2.
- There are 8 H atoms among the reactants, all in the C_3H_8 molecule, and 8 H atoms among the 4 molecules of H_2O in the products.
- There are 10 O atoms in the 5 O_2 molecules on the left side of the equation and 10 O atoms on the right side. The 10 O atoms in the products are present in 3 CO_2 molecules and 4 H_2O molecules.

Like mathematical equations, the left side of a chemical equation must be equivalent to the right side. Chemical equations are **balanced** in terms of atoms:

A correctly written chemical equation has equal numbers of each kind of atom on both sides of the equation.

As was just seen, the chemical equation being discussed has 3 carbon atoms, 8 hydrogen atoms and 10 oxygen atoms on both the left and right sides of the equation. Therefore, the equation is balanced. Balancing a chemical equation is a very important operation that is discussed in the next section.

Symbols Used in Chemical Equations

Several symbols are used in chemical equations. The two sides of the equation may be separated by an arrow, $\rightarrow$ or a double arrow, $\leftarrow\!\!\rightarrow$. The double arrow denotes a reversible reaction, that is, one that can go in either direction. The physical state (see Section 2.5) of a reaction component is indicated by letters in parentheses immediately following the formula. Therefore, (*s*) stands for a solid, (*l*) for a liquid (*g*) for a gas, and (*aq*) for a substance dissolved in aqueous (water) solution. An arrow pointing up, $\uparrow$, immediately after the formula of a product indicates that the product is evolved as a gas, whereas $\downarrow$ shows that it is a precipitate (solid forming from a reaction in solution and settling to the bottom of the container). These two symbols are not used extensively in this book, but they are encountered in some of the older chemical literature. The symbol Δ over the arrow dividing products from reactants shows that heat is applied to the reaction. As an example of the uses of some of the symbols just defined above, consider the following reaction:

$$CaCO_3(s) + H_2SO_4(aq) \xrightarrow{\Delta} CaSO_4(s) + CO_2(g) + H_2O(l) \qquad (5.2.2)$$

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This reaction shows that solid calcium carbonate reacts with a heated solution of sulfuric acid dissolved in water to form solid calcium sulfate, carbon dioxide gas, and liquid water.

5.3 BALANCING CHEMICAL EQUATIONS

As indicated in the preceding section, a correctly written chemical equation has equal numbers of atoms of each element on both sides of the equation. Balancing a chemical equation is accomplished by placing the correct number in front of each formula in the chemical equation. However, the following must be remembered:

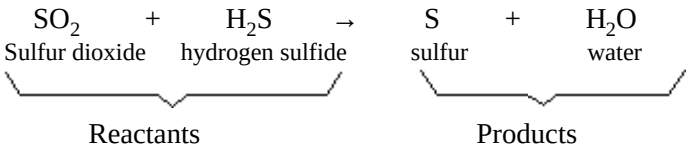
Only the numbers in front of the chemical formulas may be changed to balance a chemical equation. The chemical formulas, themselves, (subscript numbers) may not be changed in balancing the equation.

Balancing an equation is best accomplished by considering one element at a time, balancing it by changing the numbers preceding the formulas in which it is contained, then successively balancing other elements in the formulas contained in the equation.

Balancing the Equation for the Reaction of Hydrogen Sulfide with Sulfur Dioxide

As an example of how to balance a chemical equation, consider the reaction of hydrogen sulfide gas (H_2S) with sulfur dioxide (SO_2) to yield elemental sulfur (S) and water (H_2O). This reaction is the basis of the Claus process by which commercially valuable elemental sulfur is recovered from pollutant sulfur dioxide and from toxic hydrogen sulfide in "sour" natural gas. The steps used in balancing the equation are the following:

1. Write the correct formulas of the reactants and products on either side of the equation. *These must remain the same throughout the balancing process*.



2. Choose an element to balance initially, preferably one that is contained in only one reactant and one product. In this case, oxygen may be chosen. The 2 oxygen atoms in the SO_2 molecule on the left may be balanced by placing a 2 in front of the H_2O product.

$$SO_2 + H_2S \rightarrow S + 2H_2O$$

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3. Choose another element in one of the formulas involved in the preceding operation and balance it on both sides of the equation. In this case, the H in H_2O can be balanced by placing a 2 in front of H_2S.

 $$SO_2 + 2H_2S \rightarrow S + 2H_2O$$

4. Proceed to the remaining element. So far, sulfur has not yet been considered. There are 3 sulfur atoms on the left, contained in 1 SO_2 molecule and 2 H_2S molecules. We have already considered these molecules in preceding operations and should avoid changing the numbers of either one. However, sulfur can be balanced by placing a 3 in front of the S product.

 $$SO_2 + 2H_2S \rightarrow 3S + 2H_2O$$

5. Add up the numbers of each kind of element on both sides of the equation to see if they balance. In this case, it is seen that there are 3 S atoms, 4 H atoms, and 2 O atoms on both sides, so that the equation is, in fact, balanced.

Some Other Examples of Balancing Equations

Two other examples of balancing equations are considered here. The first of these is for the combustion in a moist atmosphere of aluminum phosphide, AlP, to give aluminum oxide and phosphoric acid, H_3PO_4. The unbalanced equation for this reaction is

$$AlP + O_2 + H_2O \rightarrow Al_2O_3 + H_3PO_4$$

The steps in balancing this equation are the following, starting with Al:

$$2AlP + O_2 + H_2O \rightarrow Al_2O_3 + H_3PO_4$$

Balance P:

$$2AlP + O_2 + H_2O \rightarrow Al_2O_3 + 2H_3PO_4$$

Balance H:

$$2AlP + O_2 + 3H_2O \rightarrow Al_2O_3 + 2H_3PO_4$$

Balance O:

$$2AlP + 4O_2 + 3H_2O \rightarrow Al_2O_3 + 2H_3PO_4 \qquad (5.3.1)$$

Check each element for balance:

Reactants	Products
2 Al in 2 AlP	2 Al in 1 Al_2O_3
11 O in 4 O_2 and 3 H_2O	11 O in 1 Al_2O_3 and 2 H_3PO_4
6 H in 3 H_2O	6 H in 2 H_3PO_4

The second example of balancing equations is illustrated for trimethylchlorosilane a flammable liquid used to produce high-purity silicon for semiconductor applications. Transportation accidents have resulted in spillage of this chemical and fires

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that produce carbon dioxide and a fog of silicon dioxide and hydrogen chloride dissolved in water droplets.. The unbalanced equation for this reaction is

$$(CH_3)_3SiCl + O_2 \rightarrow CO_2 + H_2O + SiO_2 + HCl$$

Si and Cl are balanced as the equation stands, so balance H:

$$(CH_3)_3SiCl + O_2 \rightarrow CO_2 + 4H_2O + SiO_2 + HCl$$

Balance C:

$$(CH_3)_3SiCl + O_2 \rightarrow 3CO_2 + 4H_2O + SiO_2 + HCl$$

Balance O:

$$(CH_3)_3SiCl + 6O_2 \rightarrow 3CO_2 + 4H_2O + SiO_2 + HCl \qquad (5.3.2)$$

Checking the quantities of each of the elements in the products and reactants shows that the equation is balanced.

In some cases, the presence of a diatomic species such as O_2 necessitates doubling quantities of everything else. As an example, consider the combustion of methane (natural gas, CH_4) in an oxygen-deficient atmosphere such that toxic carbon monoxide is produced. The unbalanced equation is

$$CH_4 + O_2 \rightarrow CO + H_2O$$

Balancing C and H gives

$$CH_4 + O_2 \rightarrow CO + 2H_2O$$

This puts a total of 3 O atoms on the right, so the addition of a single oxygen atom to the reactants side to give a total of 3 Os on the left would balance oxygen. This can be done by taking $^3/_2O_2$ to give

$$CH_4 + {}^3/_2O_2 \rightarrow CO + 2H_2O$$

Ordinarily, however, integer numbers should be used for the coefficients. The fraction can be eliminated by multiplying everything by 2 to give the balanced equation:

$$2CH_4 + 3O_2 \rightarrow 2CO + 4H_2O \qquad (5.3.3)$$

Exercise: Balance the following:

1. $Fe_2O_3 + CO \rightarrow Fe + CO_2$
2. $Fe(SO)_4 + O_2 + H_2O \rightarrow Fe(OH)_3 + H_2SO_4$

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3. $C_2H_2 + O_2 \rightarrow CO_2 + H_2O$
4. $Mg_3N_2 + H_2O \rightarrow Mg(OH)_2 + NH_3$
5. $NaAlH_4 + H_2O \rightarrow H_2 + NaOH + Al(OH)_3$
6. $Zn(C_2H_5)_2 + O_2 \rightarrow ZnO + CO_2 + H_2O$

Answers: (1) $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$, (2) $4FeSO_4 + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 4H_2SO_4$, (3) $2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$, (4) $Mg_3N_2 + 6H_2O \rightarrow 3Mg(OH)_2 + 2NH_3$ (5) $NaAlH_4 + 4H_2O \rightarrow 4H_2 + NaOH + Al(OH)_3$, (6) $2Zn(C_2H_5)_2 + 9O_2 \rightarrow 2ZnO + 4CO_2 + 10H_2O$

Summary of Steps in Balancing an Equation

Below is a summary of steps that can be followed to balance a chemical equation. Keep in mind that there is a limit to the usefulness of following a set of rules for this procedure. Ultimately, it is a matter of experience and good judgment. In general, the best sequence of steps to take is the following:

1. Express the equation in words representing the compounds, elements, and (where present) the ions participating in the reaction.
2. Write down the correct formulas of all the reactants and all the products.
3. Examine the unbalanced equation for groups of atoms, such as those in the SO_4 ion, that go through the reaction intact. Balancing is simplified by considering these atoms as a group.
4. Examine the unbalanced equation for diatomic molecules, such as O_2, whose presence may require doubling the numbers in front of the other reaction participants.
5. Choose an element, preferably one that is found in only one reactant and one product, and balance that element by placing the appropriate numbers in front of both the reactants and products involved.
6. Balance another element that appears in one of the species balanced in the preceding step.
7. Continue the balancing process, one element at a time, until all the elements have been balanced.
8. Check to make sure that the same number of atoms of each kind of element appear on both sides of the equation and that the charges from charged species (ions, whose appearance in chemical equations will be considered later) in the equation also balance on the left and right.

Exercise: The reaction of liquid hydrazine, N_2H_4, with liquid dinitrogen tetroxide, N_2O_4, to produce nitrogen gas and water is used in some rocket engines for propulsion. Balance the equation for this reaction by going through the following steps:

(a) What is the unbalanced equation for the reaction?

(b) What is the equation after balancing O?

(c) What is the equation after balancing H?

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(d) What is the equation after balancing N?

(e) How many atoms of each element are on both sides of the equation after going through these steps:

Answers: (a) $N_2O_4 + N_2H_4 \rightarrow H_2O + N_2$, (b) $N_2O_4 + N_2H_4 \rightarrow 4H_2O + N_2$, (c) $N_2O_4 + 2N_2H_4 \rightarrow 4H_2O + N_2$, (d) $N_2O_4 + 2N_2H_4 \rightarrow 4H_2O + 3N_2$, (e) 6 N, 4 O, 8 H.

5.4 WILL A REACTION OCCUR?

It is possible to write chemical equations for reactions that do not occur, or which occur only to a limited extent. This can be illustrated with a couple of examples. Consider the laboratory problem faced by a technician doing studies of plant nutrient metal ions leached from soil by water. The technician was using atomic absorption analysis, a sensitive instrumental technique for the determination of metal ions in solution. While determining the concentration of zinc ion, Zn^{2+}, dissolved in the soil leachate, the technician ran out of standard zinc solution used to provide known concentrations of zinc to calibrate the instrument, so that its readings would give known values from the sample solutions. Each liter of the standard solution contained exactly 1 mg of zinc in the form of dissolved zinc chloride, $ZnC1_2$. The technician reasoned that such a solution could be prepared by weighing out 100 mg of pure zinc metal, dissolving it in a solution of hydrochloric acid (HC1), diluting the solution to a volume of 1000 milliliters (mL), and in turn diluting 10 mL of that solution to 1000 mL to give the desired solution containing 1 mg of zinc per L. After thinking a bit, the technician came up with the equation,

$$Zn(s) + 2HCl(aq) \rightarrow H_2(g) + ZnCl_2(aq) \qquad (5.4.1)$$

to describe the chemical reaction. When the 100-mg piece of zinc metal was added to some hydrochloric acid in a flask, bubbles of hydrogen gas were evolved, the zinc dissolved as zinc chloride, and the standard solution containing the desired concentration of dissolved zinc was prepared according to the plan.

Later in the investigation, the technician ran out of standard copper solution containing 1 mg/L of copper in the form of dissolved copper(II) chloride, $CuCl_2$. The same procedure that was used to prepare the standard zinc solution was tried, with a 100-mg piece of copper wire substituted for the zinc metal. However, nothing happened to the copper metal when it was placed in hydrochloric acid. No amount of heating, stirring or waiting could persuade the copper wire to dissolve. The technician wrote the chemical equation,

$$Cu(s) + 2HCl(aq) \rightarrow H_2(g) + CuCl_2(aq) \qquad (5.4.2)$$

for the reaction analogous to that of zinc, but copper metal and hydrochloric acid simply do not react with each other. Even though a plausible chemical equation can be written for a reaction, it does not tell whether the chemical reaction will, in fact, occur. Consideration of whether particular reactions take place is considered in the realms of chemical thermodynamics and chemical equilibrium, covered in later chapters.

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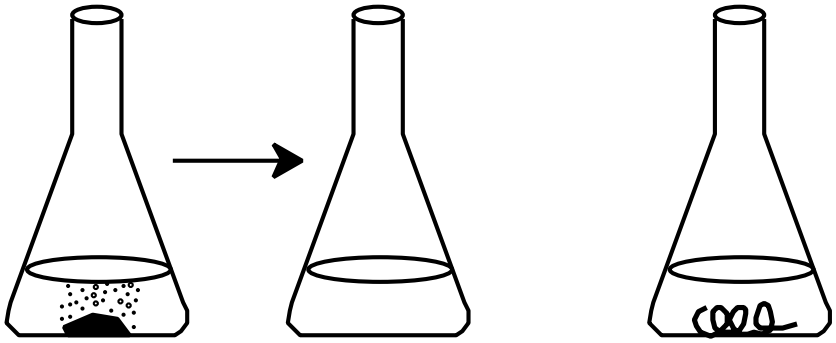


Figure 5.1 A piece of zinc metal in contact with hydrochloric acid solution reacts rapidly, giving off hydrogen gas and going into solution as $ZnCl_2$. A piece of copper metal (wire) placed in hydrochloric acid solution does not react.

5.5 HOW FAST DOES A REACTION GO?

Consider a spoonful of table sugar, sucrose, exposed to air. Will sucrose, chemical formula $C_{12}H_{22}O_{11}$, react with oxygen in the air? The following equation can be written for the chemical reaction that might occur as follows:

$$C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 12CO_2(g) + 11H_2O(l) \quad (5.5.1)$$

One may have an intuitive feeling that this reaction should occur from having seen sugar burn in a fire, or from knowing that the human body "burns" sugar to obtain energy. Furthermore, it is true that from the standpoint of energy, the atoms shown in the above equation are more stable when present as 12 molecules of CO_2 and 11 molecules of H_2O, rather than as one molecule of $C_{12}H_{22}O_{11}$ and 12 molecules of O_2. But anyone knows from experience that a spoonful of sugar can be exposed to dry air for a very long time without the occurrence of any visible change.

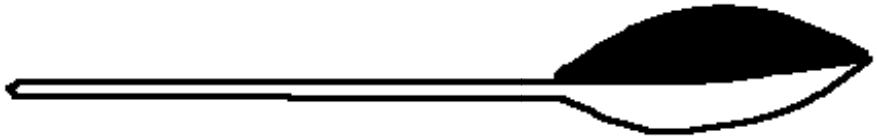


Figure 5.2: Sugar exposed to air at room temperature does not react with the oxygen in the air at a detectable rate.

The answer to the question raised above lies in the **rate of reaction**. Sucrose does, indeed, tend to react with O_2 as shown in the chemical equation above. But at room temperature, the reaction is just too slow to be significant. Of course, if the sugar were thrown into a roaring fire in a fireplace, it would burn rapidly. Special proteins known as enzymes inside of living cells can bring about the reaction of sugar and oxygen at body temperature of about 37°C, enabling the body to use the

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energy from the reaction. The enzymes themselves are not used up in the reaction, though they speed it up greatly; a substance that acts in such a manner is called a **catalyst**.

An important distinction must be made between reactions, such as that between copper and hydrochloric acid that will not occur under any circumstances, and others that "want to occur," but that are just too slow to be perceptible at moderate temperatures or in the absence of a catalyst. The latter type of reaction often does take place under the proper conditions or with a catalyst. Rates of reactions are quite important in chemistry.

5.6 CLASSIFICATION OF CHEMICAL REACTIONS

Chemical reactions may involve several kinds of processes. Reactions may consist of putting elements together to make compounds, or taking compounds apart to produce the component elements. Reactions may occur between compounds, between compounds and elements, or between ions. Many reactions involve the transfer of electrons, whereas others do not. Given these possibilities, plus others, it is helpful to categorize chemical reactions in several major classes. These are defined below.

A **combination reaction** is one in which two reactants bond together to form a single product. An example of such a reaction is provided by the burning of elemental phosphorus as one of the steps in the manufacture of phosphoric acid, a widely used industrial chemical and fertilizer ingredient. The reaction is,

$$P_4 + 5O_2(g) \rightarrow P_4O_{10} \qquad (5.6.1)$$

Elemental phosphorus, which occurs as the molecule with 4 P atoms.

Tetraphosphorus decoxide

This is one example of the many combination reactions in which two elements combine together to form a compound. The general classification, however, may be applied to combinations of two compounds or of a compound and an element to form a compound. For example, the P_4O_{10} produced in the preceding reaction is combined with water to yield phosphoric acid:

$$6H_2O + P_4O_{10} \rightarrow 4H_3PO_4 \qquad (5.6.2)$$

Phosphoric acid

A **decomposition reaction** is the opposite of a combination reaction. An example of a decomposition reaction in which a compound decomposes to form the elements in it is provided by the manufacture of carbon black. This material is a finely divided form of pure carbon, C, and is used as a filler in rubber tire manufacture and as an ingredient in the paste used to fill electrical dry cells. It is made by heating methane (natural gas) to temperatures in the range of 1260–1425°C in a special furnace, causing the following reaction to occur:

$$CH_4(g) \xrightarrow{\Delta} C(s) + 2H_2(g) \qquad (5.6.3)$$

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The finely divided carbon black product is collected in a special device called a cyclone collector, shown in Figure 5.3, and the hydrogen gas by-product is recycled as a fuel to the furnace that heats the methane. As illustrated by the preceding reaction, a reaction in which a compound is broken down into its component elements is a decomposition reaction.

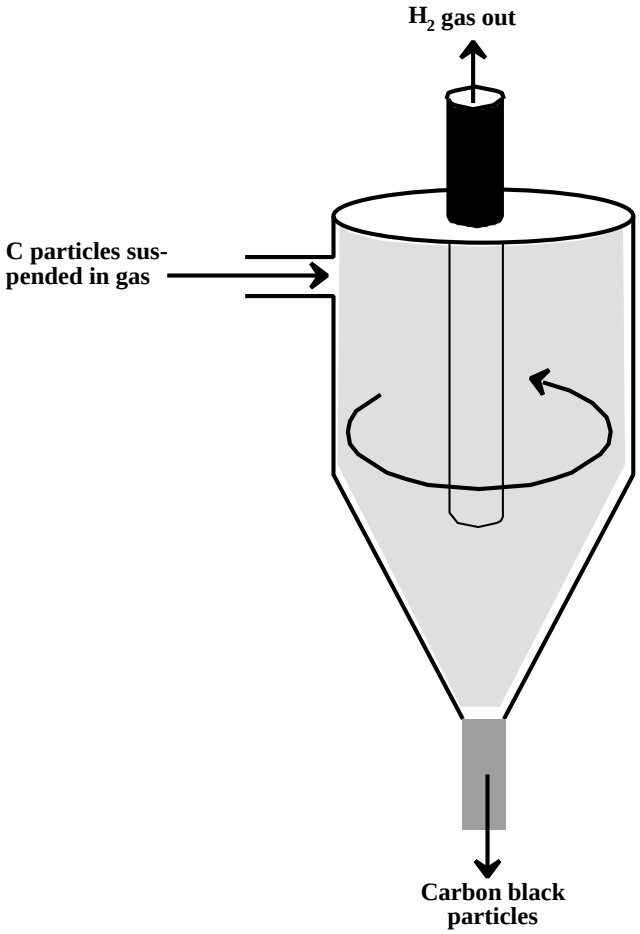


Figure 5.3. A cyclone collector is used to collect carbon black particles from a gas stream.

Decomposition reactions may also involve the breakdown of a compound to another compound and an element, or to two or more compounds. As an example of the latter, consider the reaction for the manufacture of calcium oxide, CaO, commonly called quicklime:

$$\underset{\text{Calcium carbonate (limestone)}}{CaCO_3(s)} \xrightarrow{\triangle} \underset{\text{Calcium oxide (quicklime)}}{CaO(s)} + CO_2(g) \qquad (5.6.4)$$

In this reaction, high temperatures are used to decompose limestone ($CaCO_3$) to CaO and carbon dioxide gas. This is an important reaction because quicklime, CaO, ranks

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second only to sulfuric acid in annual chemical production. It is used in the manufacture of cement, for water treatment, and in many other applications.

Substitution or **replacement** reactions occur when a component of a chemical compound is replaced by something else. For example, zinc displaces hydrogen in Reaction 5.4.1. A **double replacement** or **metathesis** reaction occurs when there is a two-way exchange of ions between compounds. This happens, for example, when a solution of sulfuric acid reacts with a solution of barium hydroxide,

$$H_2SO_4(aq) + Ba(OH)_2(aq) \rightarrow BaSO_4(s) + 2H_2O(l) \quad (5.6.5)$$

to yield solid barium sulfate and water. This reaction also falls into two other categories. Because it involves the combination of H^+ ions (from H_2SO_4) and OH^- ions (from $Ba(OH)_2$) to produce water, it is a **neutralization** reaction. This particular neutralization reaction is also a **precipitation** reaction because of the formation of a solid, $BaSO_4$. Such a solid formed by the reaction of two dissolved chemicals is called a precipitate.

The reaction of H^+ from any acid with OH^- to produce water is a neutralization reaction.

Evolution of a gas can also be used as a basis for classifying reactions. An example is provided by the treatment of industrial wastewater containing dissolved ammonium chloride, NH_4Cl. This compound is composed of the ammonium ion, NH_4^+, and the chloride ion, Cl^-. Commercially valuable byproduct ammonia gas can be recovered from such water by the addition of calcium hydroxide,

$$Ca(OH)_2(aq) + 2NH_4Cl(aq) \rightarrow 2NH_3(g) + H_2O(l) + CaCl_2(aq) \quad (5.6.6)$$

resulting in the evolution of ammonia gas, NH_3, which can be recovered.

Exercise: Classify each of the following reactions as combination, decomposition, substitution, metathesis, neutralization, precipitation, or evolution of a gas. In some cases, a reaction will fit into more than one category.

(a) $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$

(b) $2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$

(c) $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$

(d) $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

(e) $Fe(s) + CuCl_2(aq) \rightarrow Cu(s) + FeCl_2(aq)$

(f) $NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

(g) $MgCl_2(aq) + 2NaOH(aq) \rightarrow Mg(OH)_2(s) + 2NaCl(a)$

Answers: (a) Combination, (b) decomposition, evolution of a gas, (c) combination, (d) metathesis, evolution of a gas, (e) substitution, (f) neutralization, metathesis, (g) precipitation, metathesis.

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5.7 QUANTITATIVE INFORMATION FROM CHEMICAL REACTIONS

Review of Quantitative Chemical Terms

So far, chemical equations have been described largely in terms of individual atoms and molecules. Chemistry deals with much larger quantities, of course. On an industrial level, kilograms, tons, or even thousands of tons are commonly used. It is easy to scale up to such large quantities, because the relative quantities of materials involved remain the same, whether one is dealing with just a few atoms and molecules, or train-car loads of material. Before proceeding with the discussion of quantitative calculations with chemical equations, it will be helpful to consider some terms that have been defined previously:

Formula mass: The sum of the atomic masses of all the atoms in a formula unit of a compound. Although the average masses of atoms and molecules may be expressed in atomic mass units (amu or u), formula mass is generally viewed as being relative and without units.

Molar mass: Where X is the formula mass, the molar mass is X grams of an element or compound, that is, the mass in grams of 1 mole of the element or compound.

Mole: The fundamental unit for quantity of material. Each mole contains Avogadro's number (6.022×10^{23}) of formula units of the element or compound.

Formula	Formula mass	Molar mass	Number of formula units per mole
H	1.01	1.0l g/mol	6.022×10^{23} H atoms/mol
N	14.01	14.01 g/mol	6.022×10^{23} N atoms/mol
N_2	2 x 14.01 = 28.02	28.02 g/moL	6.022×10^{23} N_2 molecules/mol
NH_3	14.01 + 3 x 1.01=17.04	17.04 g/mol	6.022×10^{23} NH_3 molecules/ mol
CaO	40.08 + 16.00 =56.08	56.08 g/mol	6.022×10^{23} $\frac{\text{formula units CaO}}{\text{mol}}$*

* Since CaO consists of Ca^{2+} and O^{2-} ions, there are not really individual CaO molecules, so it is more correct to refer to a formula unit of CaO consisting of 1 Ca^{2+} ion and 1 O^{2-} ion.

Calcination of Limestone

To illustrate some of the quantitative information that may be obtained from chemical equations, consider the calcination of limestone to make quicklime for water treatment:

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$$\underset{\text{Limestone, calcium carbonate}}{CaCO_3(s)} \xrightarrow{\Delta} \underset{\text{Quicklime, calcium oxide}}{CaO(s)} + CO_2(g) \qquad (5.7.1)$$

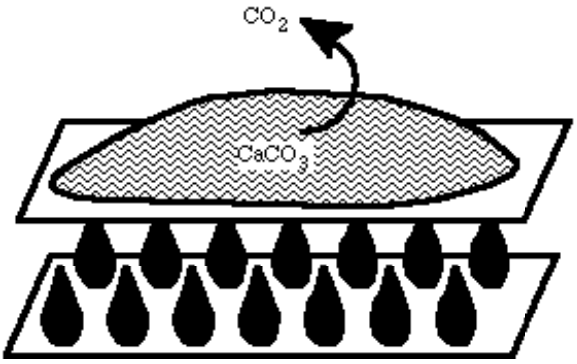


Figure 5.4 Heating calcium carbonate to a high temperature results in the production of quicklime, CaO, and the evolution of carbon dioxide. The reaction is a decomposition reaction and the process is called calcination.

The quantitative information contained in this equation can be summarized as follows:

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

At the formula unit (molecular) level		
1 formula unit	1 formula unit	1 molecule
1 Ca atom (atomic mass 40.1)	1 Ca atom	1 C atom
1 C atom (atomic mass 12.0)	1 O atom	2 O atoms
3 O atoms (atomic mass 16.0)		
100. 1 u	56.1 u	44.0 u
At the mole level		
1 mole of $CaCO_3$	1 mole of CO	1 mole of CO_2
100. 1 g of $CaCO_3$	56.1 g of CO	44.0 g of CO_2

From the quantities above, it is seen that the equation can be viewed in terms as small as the smallest number of molecules and formula units. In this case that involves simply 1 formula unit of $CaCO_3(s)$, 1 formula unit of $CaO(s)$, and 1 molecule of CO_2. This would involve a total of 1 Ca atom, 1 C atom, and 3 O atoms. From such a small scale it is possible to expand to moles by scaling up by 6.022×10^{23} (Avogadro's number), giving 100.1 g of $CaCO_3$, 56.1 g of CaO, and 44.0 g of CO_2. Actually, these quantitative relationships are applicable to any amount of matter and they enable the calculation of the amounts of material reacting and produced in a chemical reaction. Next, it is shown how these kinds of calculations are performed.

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5.8 WHAT IS STOICHIOMETRY AND WHY IS IT IMPORTANT?

Stoichiometry is the calculation of the quantities of reactants or products involved in a chemical reaction. The importance of stoichiometry can be appreciated by visualizing industrial operations that process hundreds or thousands of tons of chemicals per day. The economics of many chemical manufacturing processes are such that an unnecessary excess of only a percent or so of a reacting chemical can lead to waste that can make the operation unprofitable. Obtaining accurate values in chemical analysis, which may need to be known to within about a part per thousand, often involves highly exacting stoichiometric calculations.

Stoichiometric calculations are based upon **the law of conservation of mass**, which states that:

The total mass of reactants in a chemical reaction equals the total mass of products; Matter is neither created nor destroyed in chemical reactions.

The key to doing stoichiometric calculations correctly is the following:

The relative masses (or number of moles, number of atoms, or molecules) of the participants in a designated chemical reaction remain the same, regardless of the overall quantities of reaction participants.

The Mole Ratio Method of Stoichiometric Calculations

In a chemical reaction, there is a definite ratio between the number of moles of a particular reactant or product and the number of moles of any other reactant or product. These ratios are readily seen by simply examining the coefficients in front of the reaction species in the chemical equation. Normally, a stoichiometric calculation is made to relate the quantities of only two of the reaction participants. The objective may be to figure out how much of one reactant will react with a given quantity of another reactant. Or, a particular quantity of a product may be desired, so that it is necessary to calculate the quantity of a specific reactant needed to give the amount of product. To perform stoichiometric calculations involving only two reaction participants, it is necessary only to know the relative number of moles of each and their molar masses. The most straightforward type of stoichiometric calculation is the **mole ratio method** defined below:

*The **mole ratio method*** is *a means of performing stoichiometric calculations based upon the constant ratios of the numbers of moles of various reactants and products regardless of the overall quantity of reaction taking place.*

The mole ratio method greatly simplifies stoichiometric calculations. It can even be used to relate relative quantities of reaction participants in a series of reactions. For example, if a particular quantity of reactant is involved in a reaction followed by one or more additional reactions, the amount of a product in the final reaction is readily calculated by the mole ratio method.

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To illustrate the mole ratio method, consider a typical reaction, that of hydrogen gas and carbon monoxide gas to produce methane:

$$\underset{\substack{3\text{ moles}\\6.0\text{ g}}}{3H_2} + \underset{\substack{1\text{ mole}\\28.0\text{ g}}}{CO} \rightarrow \underset{\substack{1\text{ mole}\\16.0\text{ g}}}{CH_4} + \underset{\substack{1\text{ mole}\\18.0\text{ g}}}{H_2O} \qquad (5.8.1)$$

This reaction is called the **methanation reaction**, and is used in the petroleum and synthetic fuels industry for the manufacture of non-polluting synthetic natural gas (CH_4). From examination of the chemical equation it is easy to get the ratio of the number of moles of any reaction participant to the number of moles of any other reaction participant as shown in Table 5.1.

Table 5.1 Mole Ratios Used in Calculations with the Methanation Reaction

Equality of number of moles	Mole ratios	
$3\text{ mol } H_2 = 1\text{ mol } CO$	$\frac{3\text{ mol } H_2}{1\text{ mol } CO}$	$\frac{1\text{ mol } CO}{3\text{ mol } H_2}$
$3\text{ mol } H_2 = 1\text{ mol } CH_4$	$\frac{3\text{ mol } H_2}{1\text{ mol } CH_4}$	$\frac{1\text{ mol } CH_4}{3\text{ mol } H_2}$
$3\text{ mol } H_2 = 1\text{ mol } H_2O$	$\frac{3\text{ mol } H_2}{1\text{ mol } H_2O}$	$\frac{1\text{ mol } H_2O}{3\text{ mol } H_2}$
$1\text{ mol } CO = 1\text{ mol } CH_4$	$\frac{1\text{ mol } CO}{1\text{ mol } CH_4}$	$\frac{1\text{ mol } CH_4}{1\text{ mol } CO}$
$1\text{ mol } CO = 1\text{ mol } H_2O$	$\frac{1\text{ mol } CO}{1\text{ mol } H_2O}$	$\frac{1\text{ mol } H_2O}{1\text{ mol } CO}$
$1\text{ mol } CH_4 = 1\text{ mol } H_2O$	$\frac{1\text{ mol } CH_4}{1\text{ mol } H_2O}$	$\frac{1\text{ mol } H_2O}{1\text{ mol } CH_4}$

These ratios enable calculation of the number of moles of any reaction participant, if the number of moles of any other participant is known. For example, if it is known that 1.00 mole of H_2 reacts, the calculation of the number of moles of CH_4 produced is simply the following:

$$1.00\text{ mol } H_2 \times \frac{1\text{ mol } CH_4}{3\text{ mol } H_2} = 0.333\text{ mol } CH_4 \qquad (5.8.2)$$

Calculation of the mass of a substance requires conversion between moles and mass. Suppose that one needs to know the mass of H_2 required to produce 4.00 g of CH_4. The first step is to convert the mass of CH_4 to moles:

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$$4.00\ \text{g CH}_4 \times \frac{1\ \text{mol CH}_4}{16.0\ \text{g CH}_4} = 0.250\ \text{mol CH}_4 \qquad (5.8.3)$$

The molar mass of CH_4 is 16.0 g/mol

The next step is to multiply by the mole ratio of H_2 to CH_4:

$$0.250\ \text{mol CH}_4 \times \frac{3\ \text{mol H}_2}{1\ \text{mol CH}_4} = 0.750\ \text{mol H}_2 \qquad (5.8.4)$$

The last step is to multiply by the molar mass of H_2:

$$0.750\ \text{mol H}_2 \times \frac{2.00\ \text{g H}_2}{1\ \text{mol H}_2} = 1.50\ \text{g H}_2 \qquad (5.8.5)$$

All of these steps can be performed at once, as shown below:

$$4.00\ \text{g CH}_4 \times \frac{1\ \text{mol CH}_4}{16.0\ \text{g CH}_4} \times \frac{3\ \text{mol H}_2}{1\ \text{mol CH}_4} \times \frac{2.00\ \text{g H}_2}{1\ \text{mol H}_2} = 1.50\ \text{g H}_2 \qquad (5.8.6)$$

Several problems will be shown that illustrate the mole ratio method. First, however, it will be helpful to learn the following steps used in solving a stoichiometric problem by this method:

1. Write the balanced chemical equation for the reaction involved.
2. Identify the reactant or product whose quantity is known (known substance) and the one whose quantity is being calculated (desired substance).
3. Express the number of moles of the known substance, which usually must be calculated from its mass.
4. Multiply the number of moles of known substance times the mole ratio of desired substance to obtain the number of moles of desired substance.

 Moles desired substance = moles of known substance × mole ratio of desired substance to known substance

5. Calculate the number of grams of desired substance by multiplying its molar mass times the number of moles.

 Mass in grams of desired substance = molar mass of desired substance × moles of desired substance

To illustrate these steps, consider the preparation of ammonia, NH_3, from hydrogen gas and atmospheric nitrogen. The reaction in words is

Hydrogen plus nitrogen yields ammonia

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Insertion of the correct formulas gives,

$$H_2 \quad + \quad N_2 \quad \rightarrow \quad NH_3 \tag{5.8.7}$$

and the equation is balanced by placing the correct coefficients in front of each formula:

$$\underset{3\ \text{mol}}{3H_2} \quad + \quad \underset{1\ \text{mol}}{N_2} \quad \rightarrow \quad \underset{2\ \text{mol}}{2NH_3} \tag{5.8.8}$$

As an example, calculate the number of grams of H_2 required for the synthesis of 4.25 g of NH_3 using the following steps:

1.Calculate the number of moles of NH_3 (molar mass 17.0 g/mole).

$$\text{Mol } NH_3 = 4.25 \text{ g } NH_3 \times \frac{1 \text{ mol } NH_3}{17.0 \text{ g } NH_3} = 0.250 \text{ mol } NH_3$$

2.Express the mole ratio of H_2 to NH_3 from examination of Equation 5.8.8.

$$\frac{3 \text{ mol } H_2}{2 \text{ mol } NH_3}$$

3.Calculate the number of moles of H_2.

$$\text{Mol } H_2 = 0.250 \text{ mol } NH_3 \times \frac{3 \text{ mol } H_2}{2 \text{ mol } NH_3} = 0.375 \text{ mol } H_2$$

4.Calculate the mass of H_2.

$$0.375 \text{ mol } H_2 \times \frac{2.00 \text{ g } H_2}{1 \text{ mol } H_2} = 0.750 \text{ g } H_2$$

Once the individual steps involved are understood, it is easy to combine them all into a single calculation as follows:

$$4.25 \text{ g } H_2 \times \frac{1 \text{ mol } NH_3}{17.0 \text{ g } NH_3} \times \frac{3 \text{ mol } H_2}{2 \text{ mol } NH_3} \times \frac{2 \text{ g } H_2}{1 \text{ mol } H_2} = 0.750 \text{ g } H_2 \tag{5.8.9}$$

As a second example of a stoichiometric calculation by the mole ratio method, consider the reaction of iron(III) sulfate, $Fe(SO_4)_3$, with calcium hydroxide, $Ca(OH)_2$. This reaction is used in water treatment processes for the preparation of gelatinous iron(III) hydroxide, $Fe(OH)_3$, which settles in the water carrying solid particles with it. The iron(III) hydroxide acts to remove suspended matter (turbidity) from water. The $Ca(OH)_2$ (slaked lime) is added as a base (source of OH^- ion) to react with iron(III) sulfate. The reaction is

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$$Fe_2(SO_4)_3(aq) + 3Ca(OH)_2(aq) \rightarrow 2Fe(OH)_3(s) + 3CaSO_4(s) \qquad (5.8.10)$$

Suppose that a mass of 1000 g of iron(III) sulfate is to be used to treat a tankful of water. What mass of calcium hydroxide is required to react with the iron(III) sulfate? The steps required to solve this problem are the following:

1. Formula mass $Fe_2(SO_4)_3$ $= \underbrace{2 \times 55.8}_{\text{2 Fe atoms}} + \underbrace{3 \times 32.0}_{\text{3 S atoms}} + \underbrace{12 \times 16.0}_{\text{12 O atoms}} = 399.6$

 Formula mass $Ca(OH)_2$ $= \underbrace{1 \times 40.1}_{\text{1 Ca atom}} + \underbrace{2 \times 16.0}_{\text{2 O atoms}} + \underbrace{2 \times 1.0}_{\text{2 H atoms}} = 74.1$

2. Mol $Fe_2(SO_4)_3 = 1000 \text{ g } Fe_2(SO_4)_3 \times \dfrac{1 \text{ mol } Fe_2(SO_4)_3}{399.6 \text{ g } Fe_2(SO_4)_3}$

3. Mole ratio $= \dfrac{3 \text{ mol } Ca(OH)_2}{1 \text{ mol } Fe_2(SO_4)_3}$

4. Mass of $Ca(OH)_2 = 1000 \text{ g } Fe_2(SO_4)_3 \times \dfrac{1 \text{ mol } Fe_2(SO_4)_3}{400 \text{ g } Fe_2(SO_4)_3} \times \dfrac{3 \text{ mol } Ca(OH)_2}{1 \text{ mol } Fe_2(SO_4)_3} \times$

 $$\frac{74.1 \text{ g } Ca(OH)_2}{1 \text{ mol } Ca(OH)_2} = 556 \text{ g } Ca(OH)_2$$

Exercise: Gelatinous aluminum hydroxide for the treatment of water can be generated by the following reaction with sodium bicarbonate:

$$Al_2(SO_4)_3(aq) + 6NaHCO_3(aq) \rightarrow 2Al(OH)_3(s) + 3Na_2SO_4(aq) + 6CO_2(g)$$

Calculate the mass in kg of $NaHCO_3$ required to react with and precipitate 80.0 g of $Al_2(SO_4)_3$.

Answer: The molar mass of $NaHCO_3$ is 72.0 and that of $Al_2(SO_4)_3$ is 342.3. From the above reaction it is seen that 6 mol of $NaHCO_3$ are required per mol of $Al_2(SO_4)_3$. Therefore, the calculation is

$$\text{Mass of } NaHCO_3 = 80 \text{ g } Al_2(SO_4)_3 \times \frac{1 \text{ mol } Al_2(SO_4)_3}{342.3 \text{ g } Al_2(SO_4)_3} \times \frac{6 \text{ mol } NaHCO_3}{1 \text{ mol } Al_2(SO_4)_3} \times$$

$$\frac{72.0 \text{ g } NaHCO_3}{1 \text{ mol } NaHCO_3} = 101.0 \text{ g } Ca(OH)_2$$

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CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

The formation of chemical compounds, their decomposition, and their interactions with one another fall under the category of [1]_____. A chemical equation may be viewed as a [2]_____ in chemical language. Calculations of the quantities of substances consumed or produced in a chemical reaction are classified as [3]_____. The calculation of the quantity of heat involved in a reaction falls in the branch of chemistry called [4]_____. Substances on the left side of a chemical equation are called [5]_____ whereas those on the right are [6]_____. A correctly written chemical equation has equal numbers of [7]_____ on both sides of the equation. When used in a chemical equation, the symbols →, ← →, (*s*), (*l*), (*g*), (*aq*), ↑, ↓, and Δ stand for [8]_____ _____ _____ _____, respectively. Chemical formulas [9]_____ _____ in balancing chemical equations. After expressing an equation in words, the next step in balancing it is to [10]_____ _____. Balancing an equation may be simplified by considering groups of atoms that [11]_____. The presence of [12]_____ may require doubling the numbers in front of the other reaction participants. The final step in balancing an equation is [13]_____ _____ _____ _____.

Simply because it is possible to write a chemical equation for a reaction does not necessarily mean that [14]_____. Rates of reactions [15]_____ but may be increased by a [16]_____ _____. The reaction $C + O_2 \rightarrow CO_2$ is an example of a [17]_____ reaction. The reaction $2H_2O \rightarrow 2H_2 + O_2$ is an example of a [18]_____ reaction. The reaction $H_2SO_4 + Fe \rightarrow FeSO_4(s) + H_2$ is a [19]_____ reaction. A neutralization reaction is [20]_____ _____ and a precipitation reaction is [21]_____. Formula mass is [22]_____ _____. Molar mass is [23]_____ _____. Each mole of an element or compound contains [24]_____

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_____.

The molar mass of NH_3 is [25]_____ a mass that contains [26]_____ individual H atoms. For the smallest whole numbers of moles, the equation

$$CaCO_3(s) \xrightarrow{\Delta} CaO(s) + CO_2(g)$$

states that [27]_____ g of $CaCO_3$ are heated to produce [28]_____ g of CaO and [29]_____ g of CO_2. Stoichiometry is [30]_____
_____.

Stoichiometric calculations are based upon the law of conservation of mass, which states that [31]_____

_____.

The "key to doing stoichiometric calculations correctly" is the fact that [32]_____

_____.

In a chemical reaction there is a [33]_____ between the number of moles of a particular reactant or product and the number of moles of any other reactant or product. Using the mole ratio method for stoichiometric calculations, the steps involved after writing the balanced chemical equation for the reaction are [34]_____

_____.

Answers to Chapter Summary

1. chemical reactions
2. sentence
3. stoichiometry
4. thermochemistry
5. reactants
6. products
7. each kind of atom
8. division between reactants and products, reversible reaction, solid, liquid, gas, substance dissolved in water, evolution of a gas, formation of a precipitate, and application of heat
9. cannot be changed

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10. write down the correct formulas of all the reactants and all the products
11. go through the reaction intact
12. diatomic molecules, such as O_2
13. to check to make sure that the same number of atoms of each kind of element appear on both sides of the equation and that the charges from ions also balance on the left and right
14. the reaction will occur
15. vary greatly
16. catalyst
17. combination
18. decomposition
19. displacement
20. the reaction of H^+ from any acid with OH^- to produce water
21. one in which a solid forms from a reaction in solution
22. the sum of the atomic masses of all the atoms in a formula unit of a compound
23. the mass in grams of 1 mole of an element or compound
24. Avogadro's number (6.022×10^{23}) of formula units of the element or compound
25. 17.0 g/mol
26. $3 \times 6.022 \times 10^{23}$
27. 100. 1
28. 56.1
29. 44.0
30. the calculation of the quantities of reactants or products involved in a chemical reaction
31. the total mass of reactants in a chemical reaction equals the total mass of products, that is, matter is neither created nor destroyed in chemical reactions
32. The relative masses (or number of moles, number of atoms, or molecules) of the participants in a designated chemical reaction remain the same, regardless of the overall quantities of reaction participants.
33. definite ratio
34. (1) identify the reactant or product whose quantity is known and the one whose quantity is being calculated, (2) express the number of moles of the known substance, (3) multiply the number of moles of known substance times the mole ratio of desired substance to known substance to obtain the number of moles of desired substance, (4) calculate the number of grams of desired substance by multiplying its molar mass times its number of moles.

QUESTIONS AND PROBLEMS

Section 5.1. The Sentences of Chemistry

1. Describe chemical reactions and chemical equations and distinguish between them.

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Section 5.2. The Information in a Chemical Reaction

2. Briefly summarize the information in the chemical equation

 $CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2$

3. Summarize the information in the chemical equation, $H_2O(l) + Na(s) \rightarrow NaOH(aq) + H_2(g)$, including the meanings of the terms in italics.

4. What are the meanings of the following symbols in a chemical equation: $\rightarrow$, $\leftarrow \rightarrow$, $\uparrow$, $\downarrow$, Δ, (s), (l), (g), (aq)?

Section 5.3. Balancing Chemical Equations

5. A typical word statement of a chemical reaction is, "Ammonia reacts with sulfuric acid to yield ammonium sulfate." The compounds or the ions involved in them have been given earlier in this book. Using correct chemical formulas, show the unbalanced and balanced chemical equations for this reaction.

6. What is wrong with balancing $Ca + O_2 \rightarrow CaO$ as $Ca + O_2 \rightarrow CaO_2$?

7. Iron (II) sulfate dissolved in acid mine water, a pollutant from coal mines, reacts with oxygen from air according to the unbalanced equation $FeSO_4 + H_2SO_4 + O_2 \rightarrow Fe_3(SO_4)_3 + H_2O$. Examination of this equation reveals two things about groups of atoms that simplify the balancing of the equation. What are these two factors, and how can awareness of them help to balance the equation?

8. Balance the equation from Question 6.

9. Balance each of the following: (a) $C_2H_6 + O_2 \rightarrow CO_2 + H_2O$, (b) $KClO_3 \rightarrow KCl + O_2$, (c) $Ag_2SO_4 + BaI_2 \rightarrow AgI + BaSO_4$, (d) $KClO_4 + C_6H_{12}O_6 \rightarrow KCl + CO_2 + H_2O$, (e) $Fe + O_2 \rightarrow Fe_2O_3 + H_2O$, (f) $P + Cl_2 \rightarrow PCl_3$

Section 5.4. Will a Reaction Occur?

10. Having studied Section 5.4, and knowing something about silver metal and its uses, suggest what would happen if a small item of silver jewelry were placed in a solution of hydrochloric acid.

11. From the information given about Reactions 5.4.1 and 5.4.2, suggest a reaction that might occur if a piece of zinc metal were placed in a solution of $CuCl_2$. Explain. If a chemical reaction does occur, write an equation describing the reaction.

Section 5.5 How Fast Does a Reaction Go?

12. Steel wool heated in a flame and thrust into a bottle of oxygen gas burns vigorously, implying that a reaction such as $4Fe + 3O_2 \rightarrow 2Fe_2O_3$ does in fact occur. Why does a steel girder, such as one used for bridge construction, not burn when exposed to air?

13. What does a catalyst do?

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Section 5.6. Classification of Chemical Reactions

14. Classify each of the following reactions according to the categories that are given in Section 5.6:

 (a) $NaCl(l, \textit{melted liquid}) \xrightarrow[\text{current}]{\text{Electrical}} 2Na(l) + Cl_2(g)$

 (b) $Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$

 (c) $Zn(s) + CuCl_2(aq) \rightarrow Cu(s) + ZnCl_2(aq)$

 (d) $2NaOH(aq) + H_3PO_4(aq) \rightarrow Na_2HPO_4(aq) + 2H_2O(l)$

 (e) $BaCl_2(aq) + Ag_2SO_4(aq) \rightarrow BaSO_4(s) + 2AgCl(s)$

 (f) $(NH_4)_2SO_4(s) + Ca(OH)_2(s) \xrightarrow{\Delta} 2NH_3(g) + 2H_2O(g) + CaSO_4(s)$

Section 5.7. Quantitative Information from Chemical Reactions

15. Define (a) molecular mass (formula mass when the formula unit is a molecule), (b) mole, (c) molar mass.

16. What are the three main entities that can compose a formula unit of a substance?

17. A total of 7.52 g of $A1Cl_3$ contains (a) _____ moles and (b) _____ formula units of the compound.

18. A total of 336 g of methane, CH_4, contains (a) _____ moles and (b) _____ molecules of the compound.

Section 5.8. What is Stoichiometry and Why is it Important?

19. Ammonium nitrate, NH_4NO_3, can be made by a reaction between NH_3 and HNO_3. A "recipe" for the manufacture of ammonium nitrate specifies mixing 270 kg of NH_3 with 1000 kg of HNO_3. What is the significance of the relative quantities of these two ingredients?

20. What are some reasons that stoichiometric ratios of reactants are used for many industrial processes? In what cases are stoichiometric ratios not used?

21. What is the relationship constituting the basis of stoichiometry between the masses of the reactants and products in a chemical reaction?

22. In addition to the law of conservation of mass, another important stoichiometric relationship involves the proportions in mass of the reaction participants. What is this relationship?

23. Briefly define and explain the mole ratio method of stoichiometric calculations.

24. Carbon disulfide, CS_2, burns rapidly in air because of the reaction with oxygen. What is the mole ratio of O_2 to CS_2 in this reaction?

25. What is the first step required to solve a problem by the mole ratio method?

26. What is the mass (g) of NO_2 produced by the reaction of 10.44 g of O_2 with NO, yielding NO_2?

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27. Plants utilize light energy in the photosynthesis process to synthesize glucose, $C_6H_{12}O_6$, from CO_2 and H_2O by way of the reaction $6CO_2 + 6H_2O \rightarrow C_6H_{12}O_6 + 6O_2$. How many grams of CO_2 are consumed in the production of 90 g of glucose?

28. Bacteria in water utilize organic material as a food source, consuming oxygen in a process called respiration. If glucose sugar is the energy source, the reaction is $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$ (chemically, the reverse of the photosynthesis reaction in the preceding problem). At 25°C the maximum amount of oxygen in 1.00 liter of water due to dissolved air is 8.32 mg. What is the mass of glucose in mg that will cause all the oxygen in 1.50 L of water to be used up by bacterial respiration?

29. In a blast furnace, the overall reaction by which carbon in coke is used to produce iron metal from iron ore is $2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$. How many tons of C are required to produce 100 tons of iron metal?

30. The gravimetric chemical analysis of NaC1 may be carried out by precipitating dissolved chloride from solution by the following reaction with silver nitrate solution: $AgNO_3(aq) + NaCl \rightarrow AgCl(s) + NaNO_3(aq)$ If this reaction produced 1.225 g of AgCl, what was the mass of NaCl?

31. For the reaction of 100.0 g of NaOH with Cl_2, $2NaOH + Cl_2 \rightarrow NaClO + NaCl + H_2O$, give the masses of each of the products.

32. Hydrochloric acid (HCl gas dissolved in water) reacts with calcium carbonate in a piece of limestone as follows: $CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$. If 14.6 g of CO_2 are produced in this reaction, what is the total mass of reactants and the total mass of the products?.

33. Given the reaction in the preceding problem, how many moles of HC1 are required to react with 0.618 moles of $CaCO_3$?

34. Given the reaction in Problem 30, how many moles of $CaCO_3$ are required to produce 100.0 g of $CaCl_2$?

35. Silicon tetrachloride, $SiCl_4$, is used to make organosilicon compounds (silicones) and produces an excellent smokescreen for military operations. In the latter application, the $SiCl_4$ reacts with atmospheric moisture (water), $SiCl_4(g) + 2H_2O(g) \rightarrow SiO_2(s) + 4HCl(g)$ to form particles of silicon dioxide and hydrogen chloride gas. The HC1 extracts additional moisture from the atmosphere to produce droplets of hydrochloric acid which, along with small particles of SiO_2, constitute the "smoke" in the smokescreen. Air in a smokescreen was sampled by drawing 100 m^3 of the air through water to collect HCl and to cause any unreacted $SiCl_4$ to react according to the above reaction. After the sampling was completed, the water was found to contain 1.85 g of HC1. What was the original concentration of $SiCl_4$ in the atmosphere (before any of the above reactions occurred) in units of milligrams of $SiCl_4$ per cubic meter?

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36. Match each reaction below with the type of reaction

A. Combination (addition)
B. Decomposition
C. Metathetical (double displacement)
D. Neutralization

1. $2NaOH(aq) + H_2SO_4(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$
2. $Pb(NO_3)_2(aq) + H_2SO_4(aq) \rightarrow PbSO_4(s) + 2HNO_3(aq)$
3. $CuSO_4 \cdot 5H_2O(s) \xrightarrow{\Delta} CuSO_4(s) + 5H_2O(g)$
4. $4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$

37. Given atomic masses of Al 27 and O 16.0, the mass of O_2 consumed and the mass of Al_2O_3 produced when 29.5 g of Al undergo the reaction $4Al + 3O_2 \rightarrow 2Al_2O_3$ are

A. 26.2 g O_2 and 55.7 g Al_2O_3
B. 23.4 g O_2 and 49.7 g Al_2O_3
C. 28.7 g O_2 and 64.7 g Al_2O_3
D. 30.6 g O_2 and 65.1 g Al_2O_3
E. 20.3 g O_2 and49.8 g Al_2O_3

38. Given atomic masses H 1.0, S, 32.0, O 16.0, the mass of SO_2 that must react to yield 46.8 g of S by the reaction $2H_2S + SO_2 \rightarrow 3S + 2H_2O$ is

A. 35.1 g SO_2
B. 19.1 g SO_2
C. 31.2 g SO_2
D. 40.6 g SO_2
E. 28.3 g SO_2

39. Given atomic masses H 1.0, S, 32.0, O 16.0, the number of moles of H^+ ion that can be obtained from 24.0 g of H_2SO_4 is

A. 0.669 mol H^+
B. 0.490 mol H^+
C. 1.22 mol H^+
D. 0.555 mol H^+
E. 0.380 mol H^+

40. Of the following, mark the statement that is **incorrect** regarding the equation below:

$$CaCO_3(s) + H_2SO_4(aq) \xrightarrow{\Delta} CaSO_4(s) + CO_2(g) + H_2O(l)$$

A. $CaSO_4$ is dissolved in water.
B. $CaCO_3$ is a reactant.
C. CO_2 is a gas product.
D. The reaction mixture was heated.
E. H_2SO_4 was dissolved in water.

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41. Given atomic masses of H 1.0, Fe 55.8, and O 16.0, the number of *moles* of CO_2 produced when 79.8 g of Fe_2O_3 undergo the reaction $Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ are

 A. 2.56 mol of CO_2
 B. 1.36 mol of CO_2
 C. 1.50 mol of CO_2
 D. 1.14 mol of CO_2
 E. 1.62 mol of CO_2

42. Consider the combustion of tetraethyllead, $Pb(C_2H_5)_4$, formerly used as a gasoline octane booster, that burns in the presence of O_2 to give PbO,H_2O, and CO_2. What is the balanced chemical equation for this reaction? Assume that 1.00 g of tetraethyllead was burned. What mole ratio would be used to calculate the mass of H_2O produced? What mass of H_2O was produced?

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Manahan, Stanley E. "ACIDS, BASES, AND SALTS"
Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

6 ACIDS, BASES, AND SALTS

6.1 THE IMPORTANCE OF ACIDS, BASES, AND SALTS

Almost all inorganic compounds and many organic compounds can be classified as acids, bases, or salts. Some of these types of compounds were mentioned in earlier chapters and are discussed in greater detail in this chapter.

Acids, bases, and salts are vitally involved with life processes, agriculture, industry, and the environment. The most widely produced chemical is an acid, sulfuric acid. The second-ranking chemical, lime, is a base. Another base, ammonia, ranks fourth in annual chemical production. Among salts, sodium chloride is widely produced as an industrial chemical, potassium chloride is a source of essential potassium fertilizer , and sodium carbonate is used in huge quantities for glass and paper manufacture, and for water treatment.

The salt content and the acid–base balance of blood must stay within very narrow limits to keep a person healthy, or even alive. Soil with too much acid or excessive base will not support good crop growth. Too much salt in irrigation water may prevent crops from growing. This is a major agricultural problem in arid regions of the world such as the mid-East and California's Imperial Valley. The high salt content of irrigation water discharged to the Rio Grande River has been a source of dispute between the U.S. and Mexico that has been resolved to a degree by installation of a large desalination (salt removal) plant by the U.S.

From the above discussion it is seen that acids, bases and salts are important to human health and welfare. This chapter discusses their preparation, properties, and naming.

6.2 THE NATURE OF ACIDS, BASES, AND SALTS

Hydrogen Ion and Hydroxide Ion

Recall that an ion is an atom or group of atoms having an electrical charge. In discussing acids and bases 2 very important ions are involved. One of these is the

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hydrogen ion, $\mathbf{H^+}$. It is always produced by acids. The other is the **hydroxide ion**, $\mathbf{OH^-}$. It is always produced by bases. These two ions react together,

$$H^+ + OH^- \rightarrow H_2O \qquad (6.2.1)$$

to produce water. This is called a **neutralization reaction.** It is one of the most important of all chemical reactions.

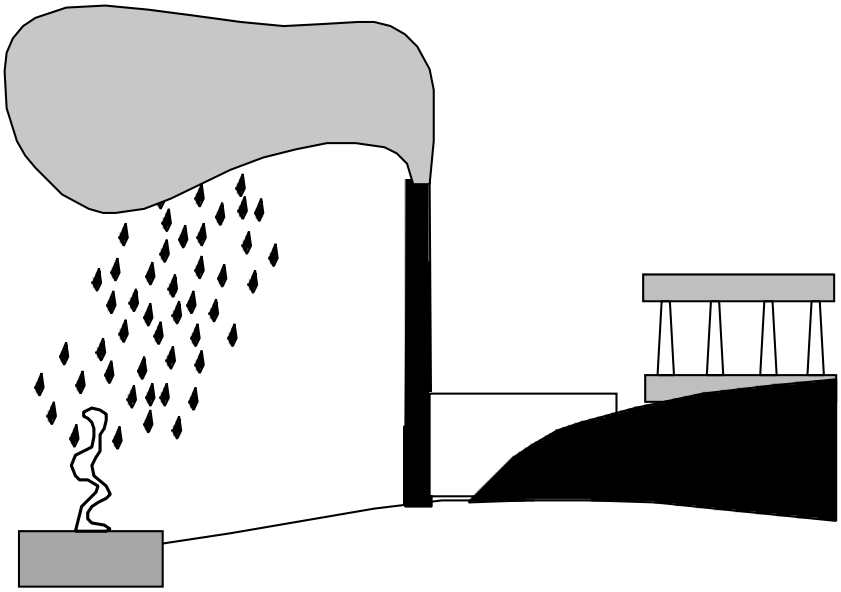
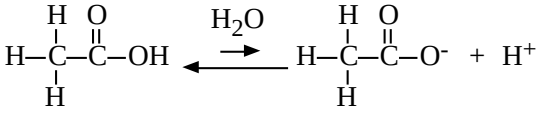


Figure 6.1 Acid rain resulting from the introduction of sulfuric, nitric, and hydrochloric acids into the atmosphere by the burning of fossil fuels damages buildings, statues, crops, and electrical equipment in some areas of the world, including parts of the northeastern U.S.

Acids

An **acid** is a substance that produces hydrogen ions. For example, HCl in water is entirely in the form of H^+ ions and Cl^- ions. These 2 ions in water form hydrochloric acid. Acetic acid, which is present in vinegar, also produces hydrogen ions in water:



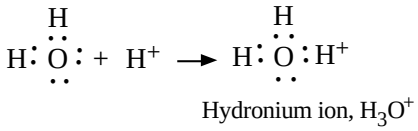
$$\qquad (6.2.2)$$

Acetic acid demonstrates two important characteristics of acids. First, many acids contain H that is not released by the acid molecule to form H^+. Of the 4 hydrogens in CH_3CO_2H, only the one bonded to oxygen is ionizable to form H^+. The second important point about acetic acid has to do with how much of it is ionized to form H^+ and acetate ion, $CH_3CO_2^{2-}$. Most of the acetic acid remains as molecules of CH_3CO_2H in solution. In a 1 molar solution of acetic acid (containing 1 mol of

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acetic acid per liter of solution) only about 0.5% of the acid is ionized to produce an acetate ion and a hydrogen ion. Of a thousand molecules of acetic acid, 995 remain as unionized CH_3CO_2H. Therefore, acetic acid is said to be a weak acid. This term will be discussed later in the chapter.

A hydrogen ion in water is strongly attracted to water molecules. Hydrogen ions react with water,



Hydronium ion, H_3O^+ (6.2.3)

to form H_3O^+ or clusters with even more water molecules such as $H_5O_2^+$ or $H_7O_3^+$. The hydrogen ion in water is frequently shown as H_3O^+. In this book, however, it is simply indicated as H^+.

Bases

A **base** is a substance that produces hydroxide ion and/or accepts H^+. Many bases consist of metal ions and hydroxide ions. For example, solid sodium hydroxide dissolves in water,

$$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq) \qquad (6.2.4)$$

to yield a solution containing OH^- ions. When ammonia gas is bubbled into water, a few of the NH_3 molecules remove hydrogen ion from water and produce ammonium ion, NH_4^+, and hydroxide ion as shown by the following reaction:

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad (6.2.5)$$

Only about 0.5% of the ammonia in a 1M solution goes to NH_4^+ and OH^-. Therefore, as discussed later in the chapter, NH_3 is called a **weak base**.

Salts

Whenever an acid and a base are brought together, water is always a product. But a negative ion from the acid and a positive ion from the base are always left over as shown in the following reaction:

$$\underset{\text{hydrochloric acid}}{H^+ + Cl^-} + \underset{\text{sodium hydroxide}}{Na^+ + OH^-} \rightarrow \underset{\text{sodium chloride}}{Na^+ + Cl^-} + \underset{\text{water}}{H_2O} \qquad (6.2.6)$$

Sodium chloride dissolved in water is a solution of a **salt**. A salt is made up of a positively charged ion called a *cation* and a negatively charged ion called an *anion*. If the water were evaporated, the solid salt made up of cations and anions would remain as crystals. A salt is a chemical compound made up of a cation (other than H^+) and an anion (other than OH^-).

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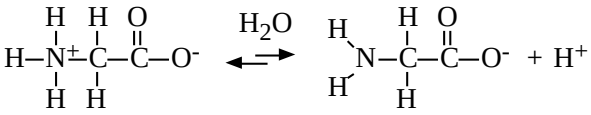
Amphoteric Substances

Some substances, called **amphoteric substances**, can act both as an acid and a base. The simplest example is water. Water can split apart to form a hydrogen ion and a hydroxide ion.

$$H_2O \rightarrow H^+ + OH^- \tag{6.2.7}$$

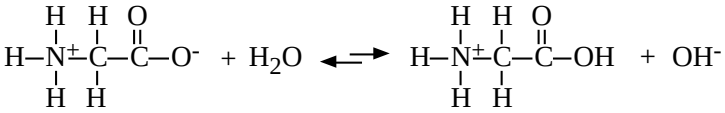
Since it produces a hydrogen ion, water is an acid. However, the fact that it produces a hydroxide ion also makes it a base. This reaction occurs only to a very small extent. In pure water only one out of 10 million molecules of water is in the form of H^+ and OH^-. Except for this very low concentration of these two ions that can exist together, H^+ and OH^- react strongly with each other to form water.

Another important substance that can be either an acid or base is glycine. Glycine is one of the amino acids that is an essential component of the body's protein. It can give off a hydrogen ion



(6.2.8)

or it can react with water to release a hydroxide ion from the water:



(6.2.9)

Metal Ions as Acids

Some metal ions are acids. As an example, consider iron(III) ion, Fe^{3+}. This ion used to be commonly called ferric ion. When iron(III) chloride, $FeCl_3$, is dissolved in water,

$$FeCl_3 + 6H_2O \rightarrow Fe(H_2O)_6^{3+} + 3Cl^- \tag{6.2.10}$$

it produces chloride ions and triply charged iron(III) ions. Each iron(III) ion is bonded to 6 water molecules. The iron(III) ion surrounded by water is called a **hydrated ion**. This hydrated iron(III) ion can lose hydrogen ions and form a slimy brown precipitate of iron(III) hydroxide, $Fe(OH)_3$:

$$Fe(H_2O)_6^{3+} \rightarrow Fe(OH)_3 + 3H_2O + 3H^+ \tag{6.2.11}$$

It is this reaction that is partly responsible for the acid in iron-rich acid mine water. It is also used to purify drinking water. The gelatinous $Fe(OH)_3$ settles out, carrying the impurities to the bottom of the container, and the water clears up.

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Salts that Act as Bases

Some salts that do not contain hydroxide ion produce this ion in solution. The most widely used of these is sodium carbonate, Na_2CO_3, which is commonly known as soda ash. Millions of pounds of soda ash are produced each year for the removal of hardness from boiler water, for the treatment of waste acid, and for many other industrial processes. Sodium carbonate reacts in water

$$\underset{\text{sodium carbonate}}{2Na^+ + CO_3^{2-}} + H_2O \rightarrow \underset{\text{sodium bicarbonate}}{Na^+ + HCO_3^-} + \underset{\text{sodium hydroxide}}{Na^+ + OH^-} \quad (6.2.12)$$

to produce hydroxide ion. If H^+, such as from hydrochloric acid, is already present in the water, sodium carbonate reacts with it as follows:

$$\underset{\text{sodium carbonate}}{2Na^+ + CO_3^{2+}} + \underset{\text{hydrochloric acid}}{H^+ + Cl^-} \rightarrow \underset{\text{sodium chloride}}{Na^+ + Cl^-} + \underset{\text{sodium bicarbonate}}{Na^+ + HCO_3^-} \quad (6.2.13)$$

Salts that Act as Acids

Some salts act as acids. Salts that act as acids react with hydroxide ions. Ammonium chloride, NH_4Cl, is such a salt. This salt is also called "sal ammoniac." As a "flux" added to solder used to solder copper plumbing or automobile radiators, ammonium chloride dissolves coatings of corrosion on the metal surfaces so that the solder can stick. In the presence of a base, NH_4Cl reacts with the hydroxide ion

$$\underset{\text{ammonium chloride}}{NH_4^+ + Cl^-} + \underset{\text{sodium hydroxide}}{Na^+ + OH^-} \rightarrow NH_3 + H_2O + \underset{\text{sodium chloride}}{Na^+ + Cl^-} \quad (6.2.14)$$

to produce ammonia gas and water.

6.3 CONDUCTANCE OF ELECTRICITY BY ACIDS, BASES, AND SALTS IN SOLUTION

When acids, bases, or salts are dissolved in water, charged ions are formed. When HCl gas is dissolved in water,

$$HCl(g) \xrightarrow{\text{Water}} H^+(aq) + Cl^-(aq) \quad (6.3.1)$$

all of it goes to H^+ and Cl^- ions. Acetic acid in water also forms a few ions,

$$CH_3CO_2H \xrightarrow{\text{Water}} H^+ + CH_3CO_2^- \quad (6.3.2)$$

but most of it stays as CH_3CO_2H. Sodium hydroxide in water is all in the form of Na^+ and OH^- ions. The salt, NaCl, is all present as Na^+ and Cl^- ions in water.

One of the most important properties of ions is that they conduct electricity in water. Water containing ions from an acid, base, or salt will conduct electricity much like a metal wire. Consider what would happen if very pure distilled water were

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made part of an electrical circuit as shown in Figure 6.2. The light bulb would not glow at all. This is because pure water does not conduct electricity. However, if a solution of salt water, such as oil well brine, is substituted for the distilled water, the bulb will glow brightly, as shown in Figure 6.2. Salty water conducts electricity because of the ions that it contains. Even tap water has some ions dissolved in it, which is why one may experience a painful, even fatal, electric shock by touching an electrical fixture while bathing.

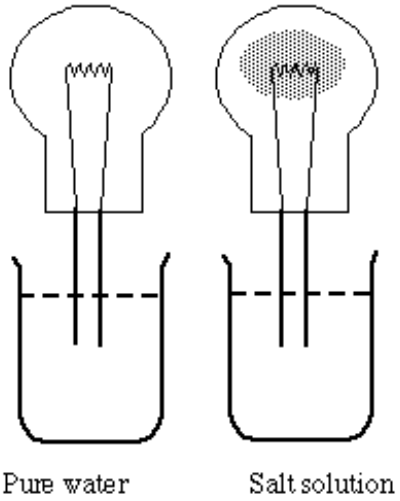


Figure 6.2 Pure water does not conduct electricity, whereas water containing dissolved salt conducts electricity very well.

Electrolytes

Materials that conduct electricity in water are called **electrolytes**. These materials form ions in water. The charged ions allow the electrical current to flow through the water. Materials, such as sugar, that do not form ions in water are called nonelectrolytes. Solutions of nonelectrolytes in water do not conduct electricity. A solution of brine conducts electricity very well because it contains dissolved NaCl. All of the NaCl in the water is in the form of Na^+ and Cl^-. The NaCl is completely ionized, and it is a strong electrolyte. An ammonia water solution (used for washing windows) does not conduct electricity very well. That is because only a small fraction of the NH_3 molecules react,

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \qquad (6.3.3)$$

to form the ions that let electricity pass through the water. Ammonia is a weak electrolyte. (Recall that it is also a weak base.) Nitric acid, HNO_3 is a strong electrolyte because it is completely ionized to H^+ and NO_3^- ions. Acetic acid is a weak electrolyte, as well as a weak acid. The base, sodium hydroxide, is a strong electrolyte. All salts are strong electrolytes because they are always completely ionized in water. Acids and bases can be weak or strong electrolytes.

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In the laboratory, the strength of an electrolyte can be measured by how well it conducts electricity in solution, as shown in Figure 6.3. The ability of a solution to conduct electrical current is called its **conductivity**.

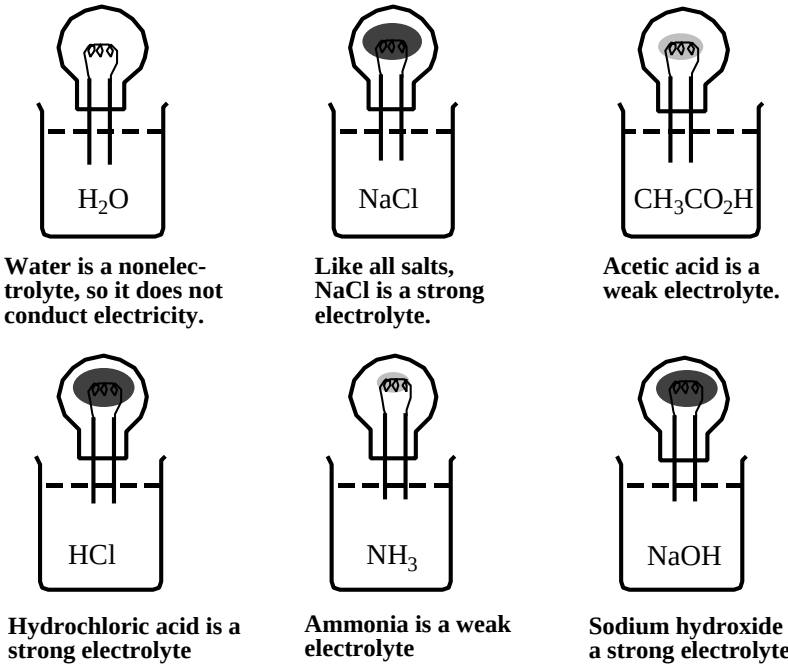


Figure 6.3 The electrical conductivity of a solution can be determined by placing the solution in an electrical circuit and observing how well electricity is conducted by the solution. **Strong electrolytes** conduct electricity well; **weak electrolytes** conduct it poorly. This principle is used in water analysis to determine the total salt concentrations in water.

When electricity is passed through solutions of acids, bases, or salts, chemical reactions occur. One such reaction is the breakdown of water to hydrogen and oxygen. Electricity passing through a solution is widely used to separate and purify various substances.

6.4. DISSOCIATION OF ACIDS AND BASES IN WATER

It has already been seen that acids and bases come apart in water to form ions. When acetic acid splits up in water,

$$CH_3CO_2H \rightarrow CH_3CO_2^- + H^+ \qquad (6.4.1)$$

it forms hydrogen ions and acetate ions. The process of forming ions is called **ionization**. Another term is commonly employed. When the acetic acid molecule comes apart, it is said to **dissociate**. The process is called **dissociation**.

There is a great difference in how much various acids and bases dissociate. Some, like HCl or NaOH, are completely dissociated in water. Because of this, hydrochloric acid is called a **strong acid**. Sodium hydroxide is a **strong base**. Some acids such as acetic acid are only partly dissociated in water. They are called weak

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acids. Ammonia, NH_3, reacts only a little bit in water to form an ammonium ion (NH_4^+) and a hydroxide ion (OH^-). It is a weak base.

The extent of dissociation is a very important property of an acid or base. The 3% or so acetic acid solution used to make up oil and vinegar salad dressing lends a pleasant taste to the lettuce and tomatoes. There is not much of the H^+ ion in the acetic acid. If 3% HCl had been used instead, nobody could eat the salad. All of the H in HCl is in the form of H^+, and a 3% solution of hydrochloric acid is very sour indeed. Similarly, a several percent solution of NH_3 in water makes a good window-washing agent, helping to dissolve grease and grime on the window surface. If a similar concentration of sodium hydroxide were used to clean windows, they would soon become permanently fogged because the OH^- in the strong base eventually reacts with glass and etches it. However, sodium hydroxide solutions are used to clean ovens, where a very strong base is required to break down the charred, baked-on grease.

Table 6.1 shows some acids and the degree to which they are dissociated. It allows comparison of the strengths of these acids.

Table 6.1 Dissociation of Acids

Acid formula	Acid name	Common uses	Percent Dissociated in 1 M solution	Strength
H_2SO_4	Sulfuric	Industrial chemical	100	Strong
HNO_3	Nitric	Industrial chemical	100	Strong
H_3PO_4	Phosphoric	Fertilizer, food additive	8	Moderately weak
$H_3C_6H_5O_7$	Citric	Fruit drinks	3	Weak
CH_3CO_2H	Acetic	Foods, industry	0.4	Weak
HClO	Hypochlorous	Disinfectant	0.02	Weak
HCN	Hydrocyanic	Very poisonous industrial chemical, electroplating waste	0.002	Very weak
H_3BO_4	Boric acid	Antiseptic, ceramics	0.002	Very weak

The percentage of acid molecules that are dissociated depends upon the concentration of the acid. The lower the concentration, the higher the percentage of dissociated molecules. This may be understood by looking again at the reaction,

$$CH_3CO_2H \rightarrow CH_3CO_2^- + H^+ \qquad (6.4.2)$$

for the dissociation of acetic acid. At high concentrations, there will be more crowding together of H^+ and $CH_3CO_2^-$ ions. This forces them back together to form CH_3CO_2H again. At low concentrations, there are fewer H^+ and $CH_3CO_2^-$ ions. They are more free to roam around the solution alone, and there is less pressure for them

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to form CH_3CO_2H. It is somewhat like the seating which occurs on a bus. If there are few passengers, they will spread out and not sit next to each other, that is, they will be dissociated. If there are many passengers, they will, of course, have to occupy adjacent seats.

An idea of the effect of concentration upon the dissociation of a weak acid can be obtained from the percentage of acid molecules that have dissociated to ions at several different concentrations. This is shown for acetic acid in Table 6.2.

Table 6.2 Percent Dissociation of Acetic Acid at Various Concentrations

Total acetic acid concentration	Percent dissociated to H^+ and $CH_3CO_2^-$
1 mol/liter	0.4
0.1 mol/liter	1.3
0.01 mol/liter	4.1
1×10^{-3} mol/liter	12
1×10^{-4} mol/liter	34
1×10^{-5} mol/liter	71
1×10^{-6} mol/liter	95
1×10^{-7} mol/liter	99

Table 6.2 shows that, in a 1 M solution, less than 1% of acetic acid is dissociated. In a one-thousandth M (0.001 M) solution, 12 out of 100 molecules of acetic acid are in the form of H^+ and acetate ions. In a one-millionth M (0.000001 M) solution only 5 out of 100 acetic acid molecules are present as CH_3CO_2H.

It is important to know the difference between the strength of an acid or base in solution and the concentration of the solution. A strong acid is one that is all in the form of H^+ ions and anions. It may be very concentrated or very dilute. A weak acid does not give off much H^+ to water solution. It may also range in concentration from a very dilute solution to a very concentrated one. Similar arguments apply to bases.

6.5 THE HYDROGEN ION CONCENTRATION AND BUFFERS

It is important to make the distinction between the concentration of H^+ and the concentration of an acid. To show this difference, compare 1 M solutions of acetic acid and hydrochloric acid. The concentration of H^+ in a 1 M solution of CH_3CO_2H is only 0.0042 mole/liter. The concentration of H^+ in a 1 M solution of HCl is 1 mole/liter. A liter of a 1 M solution of HCl contains 240 as many H^+ ions as a liter of a 1 M solution of acetic acid.

Consider, however, the amount of NaOH that will react with 1.00 liter of 1.00 M acetic acid. The reaction is

$$\underset{\text{Acetic acid}}{CH_3CO_2H} + Na^+ + OH^- \rightarrow Na^+ + \underset{\text{Sodium acetate}}{CH_3CO_2^-} + H_2O \qquad (6.5.1)$$

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Exactly 1.00 mole of NaOH reacts with the 1.00 mole of acetic acid contained in a liter of a 1.00 M solution of this acid. Exactly the same amount of NaOH reacts with the HCl in 1.00 liter of 1.00 M HCl.

$$\underset{\text{hydrochloric acid}}{H^+ + Cl^-} + \underset{\text{sodium hydroxide}}{Na^+ + OH^-} \rightarrow \underset{\text{sodium chloride}}{Na^+ + Cl^-} + H_2O \qquad (6.5.2)$$

Therefore, even though acetic acid is a weaker acid than hydrochloric acid, equal volumes of each, with the same molar concentration, will react with the same number of moles of base.

In many systems the concentration of H^+ is very important. For a person to remain healthy the H^+ concentration in blood must stay within a very narrow range. If the H^+ concentration is too high in a boiler system, the pipes may become corroded through in a short time. If the H^+ concentration becomes too high or too low in a lake, plant and animal life cannot thrive in it.

Buffers

Fortunately, there are mixtures of chemicals that keep the H^+ concentration of a solution relatively constant. Reasonable quantities of acid or base added to such solutions do not cause large changes in H^+ concentration. Solutions that resist changes in H^+ concentration are called **buffers**.

To understand how a buffer works, consider a typical buffer system. A solution containing both acetic acid and sodium acetate is a good buffer. The acetic acid in the solution is present as undissociated CH_3CO_2H. The H^+, which is in solution, is there because a very small amount of the CH_3CO_2H has dissociated to H^+ and $CH_3CO_2^-$ ions. The sodium acetate is present as Na^+ ion and $CH_3CO_2^-$ ion. If some base, such as NaOH, is added, some of the acetic acid reacts.

$$CH_3CO_2H + Na^+ + OH^- \rightarrow \underset{\text{Sodium acetate}}{Na^+ + CH_3CO_2^-} + H_2O \qquad (6.5.3)$$

This reaction changes some of the acetic acid to sodium acetate, but it does not change the hydrogen ion concentration much. If a small amount of hydrochloric acid is added to the buffer mixture of acetic acid and sodium acetate, some of the sodium acetate is changed to acetic acid.

$$\underset{\text{sodium acetate}}{Na^+ + CH_3CO_2^-} + \underset{\text{hydrochloric acid}}{H^+ + Cl^-} \rightarrow CH_3CO_2H + Na^+ + Cl^- \qquad (6.5.4)$$

The acetate ion acts like a sponge for H^+ and prevents the concentration of the added hydrogen ion from becoming too high.

Buffers can also be made from a mixture of a weak base and a salt of the base. A mixture of NH_3 and NH_4Cl is such a buffer. Mixtures of two salts can be buffers. A mixture of NaH_2PO_4 and Na_2HPO_4 is a buffer made from salts. It is one of the very common phosphate buffers, such as those that occur in body fluids.

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6.6 pH AND THE RELATIONSHIP BETWEEN HYDROGEN ION AND HYDROXIDE ION CONCENTRATIONS

Because of the fact that water itself produces both hydrogen ion and hydroxide ion

$$H_2O \rightarrow H^+ + OH^- \quad (6.6.1)$$

there is always some H^+ and some OH^- in any solution. Of course, in an acid solution, the concentration of OH^- must be very low. In a solution of base the concentration of OH^- is very high and that of H^+ is very low. There is a definite relationship between the concentration of H^+ and the concentration of OH^-. It varies a little with temperature. At 25°C (about room temperature) the following relationship applies:

$$[H^+][OH^-] = 1.00 \times 10^{-14} = K_w \quad (\text{at } 25^\circ C) \quad (6.6.2)$$

If the value of either $[H^+]$ or $[OH^-]$ is known, the value of the other can be calculated by substituting into the K_w expression. For example, in a solution of 0.100 M HCl in which $[H^+] = 0.100$ M,

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.00 \times 10^{-14}}{0.100} = 1.00 \times 10^{-13}\ M \quad (6.6.3)$$

Acids, such as HCl and H_2SO_4, produce H^+ ion, whereas bases, such as sodium hydroxide and calcium hydroxide (NaOH and $Ca(OH)_2$, respectively), produce hydroxide ion, OH^-. Molar concentrations of hydrogen ion, $[H^+]$, range over many orders of magnitude and are conveniently expressed by pH defined as

$$pH = -\log[H^+] \quad (6.6.4)$$

In absolutely pure water the value of $[H^+]$ is exactly 1×10^{-7} mole/L; therefore, the pH of pure water is 7.00, and the solution is **neutral** (neither acidic nor basic). **Acidic** solutions have pH values of less than 7 and **basic** solutions have pH values of greater than 7. Table 6.3 gives some example hydrogen ion concentrations and the corresponding pH values.

As seen in Table 6.3, when the H^+ ion concentration is 1 times 10 to a power (the superscript number, such as -2, -7, etc.) the pH is simply the negative value of that power. Thus, when $[H^+]$ is 1×10^{-3}, the pH is 3; when $[H^+]$ is 1×10^{-4}, the pH is 4. That is because the log of 1×10^{-3} is -3 and that of $1x10^{-4}$ is -4. Therefore, the negative logs are 3 and 4, respectively, because the sign is reversed. What about the pH of a solution with a hydrogen ion concentration between 1×10^{-4} and 1×10^{-3}, such as 3.16×10^{-4}? Since $[H^+]$ is between 1×10^{-4} and 1×10^{-3} M, the pH is obviously going to be between 3 and 4. The pH is calculated very easily on an electronic calculater by entering 3.16×10^{-4} on the keyboard and pressing the "log" button. The log of the number is -3.50, and the pH is 3.50.

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Table 6.3 Values of $[H^+]$ and Corresponding pH Values

$[H^+]$, mol/L	pH
1.00	0.00
0.100	1.00
1.00×10^{-3}	3.00
2.25×10^{-6} $(10^{-5.65})$	5.65
1.00×10^{-7}	7.00
1.00×10^{-9}	9.00
5.17×10^{-9} $(10^{-8.29})$	8.29
1.00×10^{-13}	13.00
1.00×10^{-14}	14.00
1.00×10^{-2}	2.00

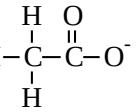
Acid-Base Equilibria

Many of the phenomena in aquatic chemistry and geochemistry involve **solution equilibrium**. In a general sense, solution equilibrium deals with the extent to which **reversible** acid-base, solubilization (precipitation), complexation, or oxidation-reduction reactions proceed in a forward or backward direction. This is expressed for a generalized equilibrium reaction

$$aA + bB \rightarrow cC + dD \tag{6.6.5}$$

There are several major kinds of equilibria in aqueous solution. The one under consideration here is acid–base equilibrium as exemplified by the ionization of acetic acid, HAc,

$$HAc \leftarrow\rightarrow H^+ + Ac^- \tag{6.6.6}$$

Ac^- represents 

for which the acid dissociation constant is

$$\frac{[H^+][Ac^-]}{[HAc]} = K = 1.75 \times 10^{-5} \quad (\text{at } 25^\circ C) \tag{6.6.7}$$

As an example of an acid–base equilibrium problem, consider water in equilibrium with atmospheric carbon dioxide. The value of $[CO_2(aq)]$ in water at 25˚C in equilibrium with air that is 350 parts per million CO_2 (close to the concentration of this gas in the atmosphere) is 1.146×10^{-5} moles/liter (M). The carbon dioxide dissociates partially in water to produce equal concentrations of H^+ and HCO_3^-:

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$$CO_2 + H_2O \leftrightarrow HCO_3^- + H^+ \quad (6.6.8)$$

so that:

$$[H^+] = [HCO_3^-] \quad (6.6.9)$$

The concentrations of H^+ and HCO_3^- are calculated from K_{a1}:

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[CO_2]} = \frac{[H^+]^2}{1.146 \times 10^{-5}} = 4.45 \times 10^{-7} \quad (6.6.10)$$

$$[H^+] = \frac{K_{a1}[CO_2^-]}{[HCO_3^-]} = \frac{[H^+]^2}{1.146 \times 10^{-5}} = 4.45 \times 10^{-7} \quad (6.6.11)$$

Since $[H^+] = [HCO_3^-]$, this relationship simplifies to

$$[H^+] = [HCO_3^-] = (1.146 \times 10^{-5} \times 4.45 \times 10^{-7})^{1/2} = 2.25 \times 10^{-6} \quad (6.6.12)$$

$$pH = 5.65$$

This calculation explains why pure water that has equilibrated with the unpolluted atmosphere is slightly acidic, with a pH somewhat less than 7.

6.7 PREPARATION OF ACIDS

Acids can be prepared in several ways. In discussing their preparation, it is important to keep in mind that acids usually contain nonmetals. All acids either contain ionizable hydrogen or produce it when dissolved in water. Furthermore, the hydrogen has to be ionizable; it must have the ability to from H^+ ion. Finally, more often than not, acids contain oxygen.

A simple way to make an acid is to react hydrogen with a nonmetal that forms a compound with hydrogen that will form H^+ ion in water. Hydrochloric acid can be made by reacting hydrogen and chlorine

$$H_2 + Cl_2 \rightarrow 2HCl \quad (6.7.1)$$

and adding the hydrogen chloride product to water. Other acids that consist of hydrogen combined with a nonmetal are HF, HBr, HI, and H_2S. Hydrocyanic acid, HCN, is an “honorary member” of this family of acids, even though it contains three elements.

Sometimes a nonmetal reacts directly with water to produce acids. The best example of this is the reaction of chlorine with water

$$Cl_2 + H_2O \rightarrow HCl + HClO \quad (6.7.2)$$

to produce hydrochloric acid and hypochlorous acid.

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Many very important acids are produced when nonmetal oxides react with water. One of the best examples is the reaction of sulfur trioxide with water

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad (6.7.3)$$

to produce sulfuric acid. Other examples are shown in Table 6.4.

Table 6.4 Important Acids Produced when Nonmetal Oxides React with Water

Oxide reacted	Acid formula	Acid Name	Use and Significance of Acid
SO_3	H_2SO_4	Sulfuric	Major industrial chemical, constituent of acid rain
SO_2	H_2SO_3	Sulfurous	Paper making, scrubbed from stack gas containing SO_2
N_2O_5	HNO_3	Nitric	Synthesis of chemicals, constituent of acid rain
N_2O_3	HNO_2	Nitrous	Unstable, toxic to ingest, few uses
P_4O_{10}	H_3PO_4	Phosphoric	Fertilizer, chemical synthesis

Volatile acids—those that evaporate easily—can be made from salts and nonvolatile acids. The most common nonvolatile acid so used is sulfuric acid, H_2SO_4. When solid NaCl is heated in contact with concentrated sulfuric acid,

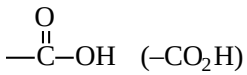
$$2NaCl(s) + H_2SO_4(l) \rightarrow 2HCl(g) + Na_2SO_4(s) \quad (6.7.4)$$

HCl gas is given off. This gas can be collected in water to make hydrochloric acid. Similarly when calcium sulfite is heated with sulfuric acid,

$$CaSO_3(s) + H_2SO_4(l) \rightarrow CaSO_4(s) + SO_2(g) + H_2O \quad (6.7.5)$$

sulfur dioxide is given off as a gas. It can be collected in water to produce sulfurous acid, H_2SO_3.

Organic acids, such as acetic acid, CH_3CO_2H, have the group



attached to a hydrocarbon group. These **carboxylic acids** are discussed further in Chapter 10.

6.8 PREPARATION OF BASES

Bases can be prepared in several ways. Many bases contain metals and some metals react directly with water to produce a solution of base. Lithium, sodium, and potassium react very vigorously with water to produce their hydroxides:

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$$2K + 2H_2O \rightarrow \underset{\substack{\text{potassium hydroxide}\\ \text{(strong base)}}}{2K^+ + 2OH^-} + H_2(g) \quad (6.8.1)$$

Many metal oxides form bases when they are dissolved in water. When waste liquor (a concentrated solution of salts and materials extracted from wood) from the sulfite paper-making process is burned to produce energy and reclaim magnesium hydroxide, the magnesium in the ash is recovered as MgO. This is added to water

$$MgO + H_2O \rightarrow Mg(OH)_2 \quad (6.8.2)$$

to produce the magnesium hydroxide used with other chemicals to break down the wood and produce paper fibers. Other important bases and the metal oxides from which they are prepared are given in Table 6.5.

Table 6.5 Important Bases Produced when Metal Oxides React with Water

Oxide reacted	Base formula	Base Name	Use and Significance of Base
Li_2O	LiOH	Lithium hydroxide	Constituent of some lubricating greases
Na_2O	NaOH	Sodium hydroxide	Soap making, many industrial uses, removal of H_2S from petroleum
K_2O	KOH	Potassium hydroxide	Alkaline battery manufacture
MgO	$Mg(OH)_2$	Magnesium hydroxide	Paper making, medicinal uses
CaO	$Ca(OH)_2$	Calcium hydroxide	Water purification, soil treatment to neutralize excessive acidity

Many important bases cannot be isolated as the hydroxides but produce OH^- ion in water. A very good example is ammonia, NH_3. Ammonium hydroxide, NH_4OH, cannot be obtained in a pure form. Even when ammonia is dissolved in water, very little NH_4OH is present in the solution. However, ammonia does react with water,

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (6.8.3)$$

to give an ammonium ion and a hydroxide ion. Since only a small percentage of the ammonia molecules react this way, ammonia is a weak base.

Many salts that do not themselves contain hydroxide ion act as bases by reacting with water to produce OH^-. Sodium carbonate, Na_2CO_3, is the most widely used of these salts. When sodium carbonate is placed in water, the carbonate ion reacts with water

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \quad (6.8.4)$$

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to form a hydroxide ion and a bicarbonate ion (HCO_3^-) . Commercial grade sodium carbonate, soda ash, is used very widely for neutralizing acid in water treatment and other applications. It is used in phosphate-free detergents. It is a much easier base to handle and use than sodium hydroxide. Whereas sodium hydroxide rapidly absorbs enough water from the atmosphere to dissolve itself to make little puddles of highly concentrated NaOH solution that are very harmful to the skin, sodium carbonate does not absorb water nearly so readily. It is not as dangerous to the skin.

Trisodium phosphate, Na_3PO_4, is an even stronger base than sodium carbonate. The phosphate ion reacts with water

$$PO_4^{3-} + H_2O \rightarrow HPO_4^{2-} + OH^- \qquad (6.8.5)$$

to yield a high concentration of hydroxide ions. This kind of reaction with water is called a **hydrolysis reaction**.

Many organic compounds are bases. Most of these contain nitrogen. One of these is trimethylamine, $(CH_3)_3N$. This compound is one of several that give dead fish their foul smell. It reacts with water

$$(CH_3)_3N + H_2O \rightarrow (CH_3)_3NH^+ + OH^- \qquad (6.8.6)$$

to produce hydroxide ion. Like most organic bases it is a weak base.

6.9 PREPARATION OF SALTS

Many salts are important industrial chemicals. Others are used in food preparation or medicine. A huge quantity of Na_2CO_3 is used each year, largely to treat water and to neutralize acid. Over 1.5 million tons of Na_2SO_4 are used in applications such as inert filler in powdered detergents. Approximately 30,000 tons of sodium thiosulfate, $Na_2S_2O_3$, are used each year in developing photographic film and in other applications. Canadian mines produce more than 10 million tons of KCl each year for use as fertilizer. Lithium carbonate, Li_2CO_3, is used as a medicine to treat some kinds of manic-depressive illness. Many other examples of the importance of salts could be given.

Whenever possible, salts are obtained by simply mining them. Many kinds of salts can be obtained by evaporating water from a few salt-rich inland sea waters or from brines pumped from beneath the ground. However, most salts cannot be obtained so directly and must be made by chemical processes. Some of these processes will be discussed.

One way of making salts already discussed in this chapter is to react an acid and a base to produce a salt and water. Calcium propionate, which is used to preserve bread is made by reacting calcium hydroxide and propionic acid, $HC_3H_5O_2$:

$$Ca(OH)_2 + 2HC_3H_5O_2 \rightarrow \underset{\text{calcium propionate}}{Ca(C_3H_5O_2)_2} + 2H_2O \qquad (6.9.1)$$

Almost any salt can be made by the reaction of the appropriate acid and base.

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In some cases, a metal and a nonmetal will react directly to make a salt. If a strip of magnesium burns (explodes would be a better description) in an atmosphere of chlorine gas,

$$Mg + Cl_2 \rightarrow MgCl_2 \quad (6.9.2)$$

magnesium chloride salt is produced.

Metals react with acids to produce a salt and hydrogen gas. Calcium placed in sulfuric acid will yield calcium sulfate.

$$Ca + H_2SO_4 \rightarrow H_2(g) + CaSO_4(s) \quad (6.9.3)$$

Some metals react with strong bases to produce salts. Aluminum metal reacts with sodium hydroxide to yield sodium aluminate, Na_3AlO_3.

$$2Al + 6NaOH \rightarrow 2Na_3AlO_3 + 3H_2(g) \quad (6.9.4)$$

In cases where a metal forms an insoluble hydroxide, addition of a base to a salt of that metal can result in the formation of a new salt. If potassium hydroxide is added to a solution of magnesium sulfate

$$2KOH + MgSO_4 \rightarrow Mg(OH)_2(s) + K_2SO_4(aq) \quad (6.9.5)$$

the insoluble magnesium hydroxide precipitates out of the solution, leaving potassium sulfate salt in solution.

If the anion in a salt can form a volatile acid, a new salt can be formed by adding a nonvolatile acid, heating to drive off the volatile product, and collecting the volatile acid in water. If nonvolatile sulfuric acid is heated with NaCl,

$$H_2SO_4 + 2NaCl \rightarrow 2HCl(g) + Na_2SO_4 \quad (6.9.6)$$

HCl gas is given off and sodium sulfate remains behind.

Some metals will displace other metals from a salt. Advantage is taken of this for the removal of toxic heavy metals from water solutions of the metals' salts by reaction with a more active metal, a process called **cementation**. For example, metallic iron can be reacted with wastewater containing dissolved toxic cadmium sulfate,

$$Fe(s) + CdSO_4(aq) \rightarrow Cd(s) + FeSO_4(aq) \quad (6.9.7)$$

to isolate solid cadmium metal and leave solid cadmium metal and a new salt, iron(II) sulfate.

Finally, there are many special commercial processes for making specific salts. One such example is the widely used Solvay Process for making sodium bicarbonate and sodium carbonate. In this process, a sodium chloride solution is saturated with ammonia gas, then saturated with carbon dioxide and finally cooled. The reaction that occurs is

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$$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3(s) + NH_4Cl \quad (6.9.8)$$

and sodium bicarbonate (baking soda) precipitates from the cooled solution. When the sodium bicarbonate is heated, it is converted to sodium carbonate:

$$2NaHCO_3 + \text{heat} \rightarrow Na_2CO_3 + H_2O(g) + CO_2(g) \quad (6.9.9)$$

6.10 ACID SALTS AND BASIC SALTS

Acid Salts

Some compounds are crosses between acids and salts. Other salts are really crosses between bases and salts. The acid salts contain hydrogen ion. This hydrogen ion can react with bases. One example of this is sodium hydrogen sulfate, $NaHSO_4$, which reacts with sodium hydroxide,

$$NaHSO_4 + NaOH \rightarrow Na_2SO_4 + H_2O \quad (6.10.1)$$

to give sodium sulfate and water. Some other examples of acid salts are shown in Table 6.6.

Table 6.6 Some Important Salts

Acid salt formula	Acid salt name	Typical use
$NaHCO_3$	Sodium hydrogen carbonate	Food preparation (baking soda)
NaH_2PO_4	Sodium dihydrogen phosphate	To prepare buffers
Na_2HPO_4	Disodium hydrogen phosphate	To prepare buffers
$KH_4C_4H_4O_6$	Potassium hydrogen tartrate	Dry acid in baking powder[1]

[1] Cream of tartar baking powder consists of a mixture of potassium hydrogen tartrate and sodium hydrogen carbonate. When this mixture contacts water in a batch of dough, the reaction

$$KHC_4H_4O_6 + NaHCO_3 \rightarrow KNaC_4H_4O_6 + H_2O + CO_2(g)$$

occurs, and the small bubbles of carbon dioxide it produces cause the dough to rise.

Basic Salts

Some salts contain hydroxide ions. These are known as **basic salts**. One of the most important of these is calcium hydroxyapatite, $Ca_5OH(PO_4)_3$. Commonly known as *hydroxyapatite*, this salt occurs in the mineral rock phosphate, which is the source of essential phosphate fertilizer. The heavy metals, in particular, have a tendency to form basic salts. Many rock-forming minerals are basic salts.

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6.11 WATER OF HYDRATION

Water is frequently bound to other chemical compounds. Water bound to a salt in a definite proportion is called **water of hydration**. An important example is sodium carbonate decahydrate:

$$Na_2CO_3 \cdot 10\ H_2O$$

Sodium carbonate decahydrate

This salt is used in detergents, as a household cleaner, and for water softening. When dissolved in water, it yields a basic solution by reacting with the water to produce hydroxide ion, OH^-. Such a solution tends to dissolve grease, so it can be used as a household cleaner. Sodium carbonate decahydrate is used in detergents, because they work best in basic solutions. The carbonate ion from this salt reacts with calcium ion (which causes water hardness),

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s) \qquad (6.11.1)$$

This removes hardness from the water by producing solid calcium carbonate, $CaCO_3$. Because of its ability to remove water hardness, sodium carbonate decahydrate is a good water softener, another reason that it is used in detergents. Sodium carbonate without water, Na_2CO_3, is said to be **anhydrous**. It should not be used in consumer products such as powdered detergents because of its strong attraction for water. If anhydrous Na_2CO_3 were present in a detergent that was accidentally ingested, it would draw water from the tissue in the mouth and throat, greatly increasing the harm done.

6.12 NAMES OF ACIDS, BASES, AND SALTS

Acids

Acids consisting of hydrogen and one other element are named for the element with a *hydro-* prefix and an ending of *-ic*. These acids include HF, hydrofluoric; HCl, hydrochloric; HBr, hydrobromic; and H_2S, hydrosulfuric acid. Another acid named in this manner is HCN, hydrocyanic acid.

The names of many common acids end with the suffix *-ic*, as is the case with acetic acid, nitric acid (HNO_3), and sulfuric acid. In some cases where the anion of the acid contains oxygen, there are related acids with different numbers of oxygen atoms in the anion. When this occurs, the acid with one less oxygen than the "-ic" acid has a name ending with *-ous.* For example, H_2SO_4 is sulfuric acid and H_2SO_3 is sulfurous acid. Similarly, HNO_3 is nitric acid and HNO_2 is nitrous acid. One more oxygen in the anion than the "-ic" acid is indicated by a *per-* prefix and an *-ic* suffix on the acid name. One less oxygen in the anion than in the "-ous" acid gives the acid a name with a *hypo-* prefix and an *-ous* suffix. These rules are shown for the oxyacids (acids containing oxygen in the anion) of chlorine in Table 6.7.

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Table 6.7 Names of the Oxyacids of Chlorine

Acid formula	Acid name[1]	Anion name[1,2]
$HClO_4$	*Per*chlor*ic* acid	*Per*chlor*ate*
$HClO_3$	Chlor*ic* acid	Chlor*ate*
$HClO_2$	Chloro*us* acid	Chlor*ite*
HClO	*Hypo*chloro*us* acid	*Hypo*chlor*ite*

[1] Italicized letters are used with the names only to emphasize the prefixes and suffixes.
[2] Names of anions, such as ClO_4^- formed by removal of H^+ ion from the acid.

Bases

Bases that contain hydroxide ion are named very simply by the rules of nomenclature for ionic compounds. The name consists of the name of the metal followed by hydroxide. As examples, LiOH is lithium hydroxide, KOH is potassium hydroxide, and $Mg(OH)_2$ is magnesium hydroxide.

Salts

Salts are named according to the name of the cation followed by the name of the anion. The names of the more important ions are listed in Table 6.8. One important cation, ammonium ion, NH_4^+, and a number of anions are polyatomic ions, meaning that they consist of 2 or more atoms per ion. Table 6.8 includes some polyatomic ions. Note that most polyatomic ions contain oxygen as one of the elements.

As illustrated in Table 6.8, the names of anions are based upon the names of the acids from which they are formed by removal of H^+ ions. A "*hydro -ic*" acid yields an "*-ide*" anion and, therefore, an "*-ide*" salt. For example, hydrochloric acid reacts with a base to give a chloride salt. An "*-ic*" acid yields an "*-ate*" salt; for example, calcium sulf*ate* is the salt that results from a reaction of sulfur*ic* acid with calcium hydroxide. The anion contained in an "*-ous*" acid is designated by the suffix "*-ite*" in a salt; sulfur*ous* acid, H_2SO_3 reacts with NaOH to give the salt Na_2SO_3 sodium sulfite. A "*per -ic*" acid, such as perchloric acid, reacts with a base, such as NaOH, to give a "*per -ate*" salt, for example, sodium perchlorate, $NaClO_4$. A "*hypo -ous*" acid, such as hypochlorous acid, reacts with a base, KOH, for example, to give a "*hypo -ite*" salt, such as potassium hypochlorite, KClO. Some additional examples are illustrated by the following reactions:

$$\underset{\text{perchloric acid}}{2HClO_4} + Zn(OH)_2 \rightarrow \underset{\text{zinc perchlorate}}{Zn(ClO_4)_2} + 2H_2O \qquad (6.12.1)$$

$$\underset{\text{nitric acid}}{2HNO_3} + Cu(OH)_2 \rightarrow \underset{\text{copper(II) nitrate}}{Cu(NO_3)_2} + 2H_2O \qquad (6.12.2)$$

$$\underset{\text{nitrous acid}}{HNO_2} + KOH \rightarrow \underset{\text{potassium nitrite}}{KNO_2} + H_2O \qquad (6.12.3)$$

$$\underset{\text{hypochlorous acid}}{2HClO} + Ca(OH)_2 \rightarrow \underset{\text{calcium hypochlorite}}{Ca(ClO)_2} + 2H_2O \qquad (6.12.4)$$

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Table 6.8 Some Important Ions

+1 charge	+2 charge	+3 charge	-1 charge	-2 charge	-3 charge
H^+, hydrogen	Mg^{2+}, magnesium	Al^{3+}, aluminum	H^-, hydride	O^{2-}, oxide	N^{3-} nitride
Li^+, lithium	Ca^{2+}, calcium	Fe^{3+}, iron(III)[2]	F^-, fluoride	S^{2-}, sulfide	PO_4^{3-} phosphate
Na^+, sodium	Ba^{2+}, barium	Cr^{3+}, chromium(III)	Cl^-, chloride	SO_4^{2-}, sulfate	
K^+, potassium	Fe^{2+}, iron (II)		Br^-, bromide	SO_3^{2-}, sulfite	
NH_4^+, ammonium	Zn^{2+}, zinc		I^-, iodide	CO_3^{2-}, carbonate	
Cu^+, copper (I)[1]	Cu^{2+}, copper(II)[2]		$C_2H_3O_2^-$, acetate	CrO_4^{2-}, chromate	
Ag^+, silver	Cr^{2+}, chromium(II)		OH^-, hydroxide	$Cr_2O_7^{2-}$, dichromate	
	Pb^{2+}, lead(II)[1]		CN^-, cyanide	O_2^{2-}, peroxide	
	Hg^{2+}, mercury(II)[2]		NO_3^-, nitrate	HPO_4^{2-}, monohydrogen phosphate	
	Sn^{2+}, tin(II)[2]		$H_2PO_4^-$, dihydrogen phosphate		
			HCO_3^-, hydrogen carbonate[3]		
			HSO_4^-, hydrogen sulfate[3]		
			MnO_4^-, permanganate		

1 These metals can also exist as ions with a higher charge and may also be designated by their Latin names with an *-ous* ending as follows: Cu^+, cuprous; Fe^{2+}, ferrous; Cr^{2+}, chromous; Pb^{2+}, plumbous; Mn^{2+}, manganous; Sn^{2+}, stannous.

2 These metals can also exist as ions with a lower charge and may also be designated by their Latin names with an *-ic* ending as follows: Cu^{2+}, cupric; Hg^{2+}, mercuric; Fe^{3+}, ferric; Cr^{3+}, chromic.

3 The ions HCO_3^- and HSO_4^- are known as bicarbonate and bisulfate, respectively.

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Using the information given in Table 6.8, it is possible to figure out the formulas and give the names of a very large number of ionic compounds. To do that, simply observe the following steps:

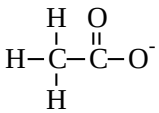
1. Choose the cation and the anion of the compound. The name of the compound is simply the name of the cation followed by the name of the anion. For example, when Fe^{3+} is the cation and SO_4^{2-} is the anion; the name of the ionic compound is iron(III) sulfate.
2. Choose subscripts to place after the cation and anion in the chemical formula of the compound such that multiplying the subscript of the cation times the charge of the cation gives a number equal in magnitude and opposite in sign from that of the product of the anion's subscript times the anion's charge. In the example of iron(III) sulfate, a subscript of 2 for Fe^{3+} gives 2 × (3+) = 6+, and a subscript of 3 for SO_4^{2-} gives 2 × (3-) = 6-, thereby meeting the condition for a neutral compound.
3. Write the compound formula. If the subscript after any polyatomic ion is greater than 1, put the formula of the ion in parentheses to show that the subscript applies to all the atoms in the ion. Omit the charges on the ions because they make the compound formula too cluttered. In the example under consideration, the formula of iron(III) sulfate is $Fe_2(SO_4)_3$.

Exercise: Match each cation in the left column below with each anion in the right column and give the formulas and names of each of the resulting ionic compounds.

(a) Na^+	(1) Br^-
(b) Ca^{2+}	(2) CO_3^{2-}
(c) Al^{3+}	(3) PO_4^{3-}

Answers: a-1, NaBr, sodium bromide; a-2, Na_2CO_3, sodium carbonate; a-3, Na_3PO_4, sodium phosphate; b-1, $CaBr_2$, calcium bromide; b-2, $CaCO_3$, calcium carbonate; b-3, $Ca_3(PO_4)_2$, calcium phosphate; c-1, $AlBr_3$, aluminum bromide; c-2, $A1_2(CO_3)_3$, aluminum carbonate; c-3, $AlPO_4$, aluminum phosphate.

The names and formulas of ionic compounds that contain hydrogen in the name and formula of the anion are handled just like any other ionic compound. Therefore, $NaHCO_3$ is sodium hydrogen carbonate, $Ca(H_2PO_4)_2$ is calcium dihydrogen phosphate, and K_2HPO_4 is sodium monohydrogen phosphate. The acetate ion, $C_2H_3O_2^-$ also contains hydrogen, but, as noted previously, its hydrogen is covalently bonded to a C atom, as shown by the structure



Acetate anion with covalently bound, nonionizable hydrogens

and cannot form H^+ ions, whereas the anions listed with hydrogen in their names can produce H^+ ion when dissolved in water.

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CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

[1]_____ ion is produced by acids and [2]_____ by bases. A neutralization reaction is [3]_____ . Hydrogen ion, H^+, in water is bonded to [4]_____ and is often represented as [5]_____. A **base** is a substance that accepts H^+ and produces hydroxide ion. Although NH_3 does not contain hydroxide ions, it undergoes the reaction [6]_____ to produce OH^- in water. The two products produced whenever an acid and a base react together are [7]_____. A salt is made up of [8]_____ _____. An amphoteric substance is one that [9]_____. In water, a metal ion is bonded to [10]_____ in a form known as a [11]_____. In terms of acid–base behavior, some metal ions act as [12]_____. In water solution sodium carbonate acts as a [13]_____ and undergoes the reaction[14]_____ _____. Salts that act as acids react with [15]_____ _____. Pure water conducts electricity [16]_____, a solution of acetic acid conducts electricity [17]_____, and a solution of HCl conducts electricity [18]_____.These differences are due to differences in concentrations of [19]_____ in the water. Materials that conduct electricity in water are called [20]_____. Materials that do not form ions in water are called [21]_____. The reaction

$$CH_3CO_2H \rightarrow CH_3CO_2^- + H^+ \qquad (6.4.1)$$

may be classified as [22]_____ or [23]_____ and when the acetic acid molecule comes apart, it is said to [24]_____. A base that is completely dissociated in water is called a [25]_____ and an acid that is only slightly dissociated is called a [26]_____. At high concentrations the percentage of dissociation of a weak acid is [27]_____ than at lower concentrations. Buffers are [28]_____ _____. A buffer can be made from a mixture of a weak base and [29]_____. The reaction that results in the production of very low concentrations of ions in even pure water is [30]_____ _____ and the relationship between the concentrations of these ions in water is [31]_____. In absolutely pure water the value of $[H^+]$ is exactly [32]_____, the pH is [33]_____, so that the solution is said to be [34]_____. Acidic solutions have pH values of [35]_____ and basic solutions have pH values of [36]_____. In a general sense solution equilibrium deals with the extent to which reversible acid-base, solubilization (precipitation), complexation, or oxidation-reduction reactions [37]_____ _____. As an example of acid-base equilibrium

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the reaction for the ionization of acetic acid, HAc, is [38]_____ for which the acid dissociation constant is [39]_____. Some ways to prepare acids are [40]_____

_____.
Some ways to prepare bases are [41]_____

_____.
The reaction of an ion with water such as

$$PO_4^{3-} + H_2O \rightarrow HPO_4^{2-} + OH^-$$

is an example of a [42]_____. The most obvious way to prepare a salt is by [43]_____. Active metals react with acids to produce [44]_____. Other than reacting with acids, some metals react with [45]_____. If the anion in a salt can form a volatile acid, a new salt can be formed by [46]_____ _____. Some metals will displace other metals from a salt. If magnesium, a highly reactive metal is added to a solution of copper sulfate, the reaction that occurs is [47]_____. $NaHSO_4$, which has an ionizable hydrogen, is an example of [48]_____, whereas $Ca_5OH(PO_4)_3$ is an example of [49]_____. The water in $CuSO_4 \cdot 5H_2O$ is called [50]_____ _____. The names of $HClO_4$, $HClO_3$, $HClO_2$, and HClO are, respectively, [51]_____.
The names of $NaClO_4$, $NaClO_3$, $NaClO_2$, and NaClO are, respectively, [52]_____ _____.
The name of a base containing a metal consists of [53]_____ _____. As examples, LiOH is lithium hydroxide, KOH is potassium hydroxide, and $Mg(OH)_2$ is magnesium hydroxide. The name of a salt is [54]_____. The names of the ions Ca^{2+}, Fe^{3+}, H^-, SO_3^{2-}, and $C_2H_3O_2^-$ are, respectively, [55]_____ _____.
In writing the formulas of ionic compounds, choose subscripts to place after the cation and anion in the chemical formula of the compound such that multiplying the subscript of the cation times the charge of the cation gives a number [56]_____ _____ and opposite in sign from that of the product of [57]_____ _____.

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Answers to Chapter Summary

1. H^+
2. OH^-
3. $H^+ + OH^- \rightarrow H_2O$
4. water molecules
5. hydronium ion, H_3O^+
6. $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$
7. water and a salt
8. a cation (other than H^+) and an anion (other than OH^-)
9. can act as either an acid or a base
10. water molecules
11. hydrated ion
12. acids
13. base
14. $2Na^+ + CO_3^{2-} + H_2O \rightarrow Na^+ + HCO_3^- + Na^+ + OH^-$
15. hydroxide ions
16. not at all
17. poorly
18. very well
19. ions
20. electrolytes
21. nonelectrolytes
22. ionization
23. dissociation
24. dissociate
25. strong base
26. weak acid
27. lower
28. solutions that resist changes in H^+ concentration
29. a salt of the base
30. $H_2O \rightarrow H^+ + OH^-$
31. $[H^+][OH^-] = 1.00 \times 10^{-14} = K_w$
32. 1×10^{-7} mole/L
33. 7.00
34. neutral
35. less than 7
36. greater than 7
37. proceed in a forward or backward direction
38. $HAc \leftrightarrow H^+ + Ac^-$
39. $\dfrac{[H^+][Ac^-]}{[HAc]} = K = 1.75 \times 10^{-5}$
40. reaction of hydrogen with a nonmetal, reaction of a nonmetal directly with water, reaction of a nonmetal oxide with water, production of volatile acids by reaction of salts of the acids with nonvolatile acids
41. reaction of active metals directly with water, reaction of metal oxides with

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water, reaction of a basic compound that does not itself contain hydroxide with water

42. hydrolysis
43. reaction of an acid with a base
44. a salt and hydrogen gas
45. strong bases
46. adding a nonvolatile acid
47. $Mg(s) + CuSO_4(aq) \rightarrow Cu(s) + MgSO_4(aq)$
48. an acid salt
49. a basic salt
50. water of hydration
51. perchloric acid, chloric acid, chlorous acid, and hypochlorous acid
52. sodium perchlorate, sodium chlorate, sodium chlorite, and sodium hypochlorite
53. the name of the metal followed by hydroxide
54. the name of the cation followed by the name of the anion
55. calcium, iron(III), hydride, sulfite, and acetate
56. equal in magnitude
57. the anion's subscript times the anion's charge

QUESTIONS AND PROBLEMS

1. Give the neutralization reaction for each of the acids in the left column reacting with each of the bases in the right column, below:

(1) Hydrocyanic acid	(a) Ammonia
(2) Acetic acid	(b) Sodium hydroxide
(3) Phosphoric acid	(c) Calcium hydroxide

2. Methylamine is an organic amine, formula $H_3C\text{-}NH_2$, that acts as a weak base in water. By analogy with ammonia, suggest how it might act as a base.
3. In a 1 molar solution of acetic acid (containing 1 mol of acetic acid per liter of solution) only about 0.5% of the acid is ionized to produce an acetate ion and a hydrogen ion. Calculate the number of moles of H^+ in a liter of such a solution.
4. What does H_3O^+ represent in water?
5. When exactly 1 mole of NaOH reacts with exactly 1 mole of H_2SO_4, the product is an acid salt. Show the production of the acid salt with a chemical reaction.
6. An amphoteric substance can be viewed as one that may either accept or produce an ion of H^+. Using that definition, explain how H_2O is amphoteric.
7. Explain how Fe^{3+} ion dissolved in water can be viewed as an acidic hydrated ion.
8. Cyanide ion, CN^-, has a strong attraction for H^+. Show how this explains why NaCN acts as a base.
9. Separate solutions containing 1 mole per liter of NH_3 and 1 mole per liter of acetic acid conduct electricity poorly, whereas when such solutions are mixed, the resulting solution conducts well. Explain.

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10. What characteristic of solutions of electrolytes enables them to conduct electricity well?

11. A solution containing 6 moles of NH_3 dissolved in a liter of solution would be relatively highly concentrated. Explain why it would not be correct, however, to describe such a solution as a "strong base" solution.

12. The dissociation of acetic acid can be represented by

 $$CH_3CO_2H \rightarrow CH_3CO_2^- + H^+$$

 Explain why this reaction can be characterized as an ionization of acetic acid. Explain on the basis of the "crowding" concept why the percentage of acetic acid molecules dissociated is less in relatively concentrated solutions of the acid.

13. A solution containing 0.1 mole of HCl per liter of solution has a low pH of 1, whereas a solution containing 0.1 mole of acetic acid per liter of solution has a significantly higher pH. Explain.

14. Explain why a solution containing both NH_3 and NH_4Cl acts as a buffer. In so doing, consider reactions of NH_3, NH_4^+ ion, H^+ ion, OH^- ion, and H_2O.

15. NaH_2PO_4 and Na_2HPO_4 dissolved in water produce $H_2PO_4^-$ and HPO_4^{2-} ions, respectively. Show by reactions of these ions with H^+ and OH^- ions why a solution consisting of a mixture of both NaH_2PO_4 and Na_2HPO_4 dissolved in water acts as a buffer.

16. What is the expression and value for K_w? What is the reaction upon which this expression is based?

17. On the basis of pH, distinguish among acidic, basic, and neutral solutions.

18. Give the pH values corresponding to each of the following values of $[H^+]$: (a) 1.00×10^{-4} mol/L, (b) 1.00×10^{-8} mol/L, (c) 5.63×10^{-9} mol/L, (d) 3.67×10^{-6} mol/L.

19. Why does solution equilibrium deal only with reversible reactions?

20. Write an equilibrium constant expression for the reaction

 $$CO_3^{2-} + H_2O \leftarrow\rightarrow HCO_3^- + OH^-$$

21. Calculate $[H^+]$ in a solution of carbon dioxide in which $[CO_2(aq)]$ is 3.25×10^{-4} moles/liter.

22. Cl_2 and F_2 are both halogens. Suggest acids that might be formed from the reaction of F_2 with H_2 and with H_2O.

23. Suggest the acid that might be formed by reacting S with H_2.

24. Suggest the acid or base that might be formed by the reaction of each of the following oxides with water: (a) N_2O_3, (b) CO_2, (c) SO_3, (d) Na_2O, (e) CaO, (f) Cl_2O.

25. Knowing that H_2SO_4 is a non-volatile acid, suggest the acid that might be formed by the reaction of H_2SO_4 with water.

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26. Acetic acid is a carboxylic acid. Formic acid is the lowest carboxylic acid, and it contains only 1 C atom per molecule. What is its formula?

27. A base can be prepared by the reaction of calcium metal with hot water. Give the reaction and the name of the base product.

28. A base can be prepared by the reaction of sodium oxide with water. Give the reaction and the name of the base product.

29. Give the reactions by which the following act as bases in water: (a) NH_3, (b) Na_2CO_3, (c) Na_3PO_4, and dimethylamine, $(CH_3)_2NH$.

30. Choosing from the reagents H_2SO_4, HCl, $Mg(OH)_2$, and LiOH give reactions that illustrate "the most straightforward" means of preparing salts.

31. Choosing from the reagents NaOH, HCl, , CaO, Mg, F_2 and Al give reactions that illustrate the preparation of salts by (a) reaction of a metal and a nonmetal that will react directly to make a salt, (b) reaction of a metal with acid, (c) reaction of a metal with strong base, (d) reaction of a salt with a nonvolatile acid, (e) cementation.

32. Describe what is meant by an acid salt.

33. Describe what is meant by a basic salt.

34. Explain how sodium carbonate decahydrate illustrates water of hydration. Why is it less hazardous to skin than is anhydrous sodium carbonate? Illustrate with a chemical reaction why it is also a basic salt.

35. Give the names of each of the following acids: (a) HBr, (b) HCN, (c) HClO, (d) $HClO_2$, (e) $HClO_3$, (f) $HClO_4$, (g) HNO_2.

36. Give the names of (a) LiOH, (b) $Ca(OH)_2$, and (c) $Al(OH)_3$.

37. Give the names of (a) $MgSO_3$, (b) NaClO, (c) $Ca(ClO_4)_2$, (d) KNO_3, (d) $Ca(NO_2)_2$

38. Match each cation in the left column below with each anion in the right column and give the formulas and names of each of the resulting ionic compounds.

(a) Li^+	(1) CN^-
(b) Ca^{2+}	(2) SO_3^{2-}
(c) Fe^{3+}	(3) NO_3^-

39. What color is litmus in (A) acid and (B) base?

40. Give the formulas of each of the following:

Magnesium acetate
Calcium monohydrogen phosphate
Aluminum sulfate
Calcium hypochlorite

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41. Using Lewis (electron-dot) structures, show the reaction between hydronium ion and hydroxide ion.

42. A common error in speaking the chemical language is to confuse acidic (pronounced uh-sid-ik) with acetic (pronounced uh-seat-ik). What is the correct meaning of each of these terms? What is the difference between ammoni*a* and ammoni*um*?

43. The following is a list that contains the names of three cations and three anions: hypochlorite, hydrogen, sodium, sulfate, calcium, nitrate. List the three cations. List the three anions. Give the formulas of nine compounds that can be made by various combinations of these.

44. Write a chemical reaction in which $NaHCO_3$ acts as an acid. Write another in which it acts as a base, remembering that if H_2CO_3 is produced in solution it largely goes to carbon dioxide gas and water.

45. Write the Lewis structure of the hydronium ion, H_3O^+.

46. Explain by chemical reactions how a mixture of $NaHCO_3$ and Na_2CO_3 in water would act as a buffer.

47. A solid known to be either NaCl or Na_2SO_4 was moistened with concentrated H_2SO_4 and heated, giving off a gas that turned moist blue litmus paper red. What was the solid?

48. Formulas of some chemical compounds are given in the lefthand column. Match the formula of each compound with its correct name in the righthand column.

CaO	Potassium sulfide
SiO_2	Dinitrogen pentoxide
K_2S	Nitrogen dioxide
$AlCl_3$	Silicon dioxide
NO_2	Potassium bromide
N_2O_5	Sodium iodide
NaI	Calcium oxide
KBr	Magnesium fluoride
MgF_2	Calcium fluoride
CaF_2	Aluminum chloride

49. Match the names in the right column with the formulas in the left column.

Na_2CO_3	Calcium sulfate
$CaSO_3$	Potassium perchlorate
$Al(OH)_3$	Sodium carbonate
$CaSO_4$	Calcium phosphate
$NaNO_2$	Aluminum hydroxide
$Ca_3(PO_4)_2$	Calcium sulfite
$NaNO_3$	Calcium hypochlorite
$Ca(ClO)_2$	Sodium nitrate
$KClO_4$	Sodium nitrite

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50. Match the names in the right column with the formulas in the left column.

K_2HPO_4	Sodium hydrogen sulfate
$KHCO_3$	Sodium hydrogen oxalate
$NaHSO_4$	Dipotassium hydrogen phosphate
KH_2PO_4	Sodium hydrogen phthalate
$NaHC_8H_4O_4$	Potassium hydrogen carbonate
$NaHC_2O_4$	Potassium dihydrogen phosphate

51. Fill in each of the following blanks with the number corresponding to the meaning of each of the prefixes. The first one is done for you as an example.

tetra __4__ mono _____ octa _____ deca _____ di _____

penta _____ hepta _____ tri _____ nona _____ sexa _____

52. Give the correct name to each of the following compounds. The first one is done for you as an example.

N_2O_5 Dinitrogen pentoxide N_2O_4 _____

NO_2 _____ N_2O_3 _____

NO _____ N_2O _____

53. Iron in a compound can also be designated as ferrous or ferric. Similarly copper (Cu) may be called cuprous or cupric. Tin (Sn) may be called stannous or stannic. Name each of the following compounds with two acceptable names. The first one is done for you as an example.

$FeCl_2$ ferrous chloride or iron (II) chloride

$FeCl_3$ _____ or _____

CuCl _____ or _____

$CuCl_2$ _____ or _____

$SnCl_2$ _____ or _____

$SnCl_4$ _____ or _____

54. Dry $CaSO_4$ absorbs enough water to yield a product with a specific number or waters of hydration. Exactly 136 g. of $CaSO_4$ exposed to humid air gained enough water to weigh exactly 172 g. What is the formula of the product with the waters of hydration?

55. In each of the following chemical reactions fill in the formula of the missing compound. The rest of the chemical equation is balanced.

$2\ N_2 + 3\ O_2 \rightarrow$ _____ (nitrogen trioxide)

$KOH + SO_2 \rightarrow$ _____ (potassium hydrogen sulfite)

$KOH + H_3PO_4 \rightarrow$ _____ (potassium dihydrogen phosphate)

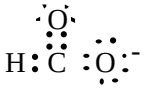
56. Give one or two examples of compounds in which each of the following prefixes or suffixes is used in the compound name.

-ic	acetic acid	hydrochloric acid
-ide	_____	_____

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-ous _____ _____
hypo- _____ _____
per- _____ _____
-ite _____ _____
-ate _____ _____

57. In this chapter, it was mentioned that a certain group was characteristic of organic acids. The Lewis structure of acetic acid was also given and it was shown how many of its Hs can form H^+ ion. The Lewis formula of the formate ion produced by the ionization of formic acid is,



From this information, explain how many ionizable hydrogens formic acid has, and why it has that number.

58. How do you explain the fact that a 0.01 M solution of HCl contains more H^+ ions than does as 0.1 M (ten-fold higher concentration) of acetic acid?

59. How is it explained that a solution of $FeCl_3$ is acidic?

60. Explain how a mixture of NH_3 and NH_4Cl dissolved in solution can act as a buffer.

61. Hydrochloric acid, HCl, is often found in rainwater in ocean coastal areas in which the atmosphere is polluted by sulfuric acid. How might this occur?

62. Classify each of the following as strong electrolytes, weak electrolytes, or nonelectrolytes: (A) Solution of NaCl, (B) vinegar, (C) pure water, (D) solution of sugar, (E) solution of HCl, (F) solution of ammonia, (G) solution of sodium hydroxide.

63. Match the value of $[H^+]$ in the left column below with the pH in the right column.

A. 1.00×10^{-8} M	1.8.37
B. 1.00×10^{-9} M	2.8.00
C. 4.28×10^{-9} M	3.7.70
D. 2.00×10^{-8} M	4.9.00

64. Exactly 1.00 mole of an acid was dissolved in 1.00 liter of water solution. The pH of the resulting solution was 2.00. Referring to Tables 6.1 and 6.3, classify the acid in regard to its strength.

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Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

7 SOLUTIONS

7.1 WHAT ARE SOLUTIONS? WHY ARE THEY IMPORTANT?

To help understand solutions, consider a simple experiment. Run some water from a faucet into a glass and examine it. Depending on the condition of the local water supply, it will probably appear clear. If tasted, it will probably not have any particularly strong flavors. Now, add a teaspoon of sugar and stir the contents of the glass; you will notice the sugar begin to disappear, and the water around the sugar will start to appear cloudy or streaked. With continued stirring, the sugar will seem to disappear completely, and the water will look as clear as it did when it came out of the tap. However, it will have a sweet taste; some of its properties have therefore been changed by the addition of sugar.

This experiment illustrates several important characteristics of chemicals and how they are used. Sugar **dissolves** in water; when this happens, a **solution** is formed. The sugar molecules were originally contained in hard, rigid sugar crystals. In water, the molecules break away from the crystals and spread throughout the liquid. The sugar is still there, but it is dissolved in the water, which is called the **solvent**. The dissolved sugar is called the **solute**; it can no longer be seen, but it can be tasted. The water appears unchanged, but it is different. It has a different taste. Some of its other properties have changed, too; for example, it now boils at a higher temperature and freezes at a lower temperature than pure water. In some cases there is readily visible evidence that a solute is present in a solvent. The solution may have a strong color, as is the case for intensely purple solutions of potassium permanganate, $KMnO_4$. It may have a strong odor, such as that of ammonia, NH_3, dissolved in water.

As illustrated in Figure 7.1, tap water itself is a solution containing many things. It has some dissolved oxygen and carbon dioxide in it. It almost certainly has some dissolved calcium compounds, making it “hard.” There may be a small amount of iron present, which causes the water to stain clothing. It contains some chlorine, added to kill bacteria. In unfavorable cases, it may even contain some toxic lead and cadmium dissolved from plumbing and the solder used to connect copper pipes.

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Thus, it is clear that many of the liquids that people come in contact with are actually solutions.

There are many examples of important and useful solutions. Sugar, for instance, must be dissolved before it can be used by the body for food. Candy, which is sugar with added flavoring, dissolves in the mouth to form a solution of sugar with saliva. The coolant in an automobile's cooling system is a solution of antifreeze in water. This solution freezes at a much lower temperature than pure water, thus preventing the liquid from freezing and cracking the engine block. A solution containing the simple sugar glucose and some other substances may be injected directly into the veins of an ill or injured person who cannot take food throught the mouth. Chemists use many different kinds of solutions that undergo chemical reactions with other kinds of chemicals. By measuring how much of solution is required to complete a reaction in a procedure called *titration*, the chemist can tell how much of a particular kind of chemical is in a solution.

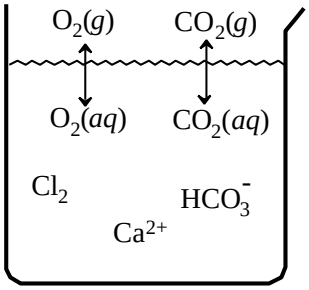


Figure 7.1 Tap water is actually a solution that contains, in small quantities, many chemical species besides H_2O.

Reactions in Solution

One of the most important properties of solutions is their ability to allow chemical species to come into close contact so that they can react. For example, if perfectly dry crystals of calcium chloride, $CaCl_2$, were mixed with dry crystals of sodium fluoride, NaF, a chemical reaction would not occur. However, if each is dissolved in separate solutions which are then mixed, a precipitation reaction occurs,

$$CaCl_2(aq) + 2NaF(aq) \rightarrow CaF_2(s) + 2NaCl(aq) \qquad (7.1.1)$$

in which calcium chloride and sodium fluoride in aqueous solution (*aq*) react to produce calcium fluoride solid (*s*) and a solution of sodium chloride. This reaction occurs because in solution the Ca^{2+} ions (from dissolved $CaCl_2$) and the F^- ions (from dissolved NaF) move around and easily come together to form CaF_2. The calcium fluoride product does not stay in solution but forms a precipitate; it is **insoluble**.

In other cases, solutions enable chemical reactions to occur that result in materials being dissolved. Some of these reactions are important in geology. Consider limestone, which is made of calcium carbonate, $CaCO_3$. Limestone does not react with dry CO_2 gas, nor is it soluble in pure water. However, when water containing dissolved CO_2 contacts limestone, a chemical reaction occurs:

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$$CaCO_3(s) + CO_2(g) + H_2O \rightarrow Ca^{2+}(aq) + 2HCO_3^-(aq) \quad (7.1.2)$$

The calcium ion and the bicarbonate ion, HCO_3^-, remain dissolved in water; this solution dissolves the limestone, leaving a cave or hole in the limestone formation. In some regions, such as parts of southern Missouri, this has occurred to such an extent that the whole area is underlain by limestone caves and potholes; these are called *karst* regions.

Solutions in Living Systems

For living things the most important function of solutions is to carry molecules and ions to and from cells. Body fluids consist of complex solutions. Digestion is largely a process of breaking down complex, insoluble food molecules to simple, soluble molecules that may be carried by the blood to the body cells, which need them for energy and production of more cell material. On the return trip the blood carries waste products, such as carbon dioxide, which are eliminated from the body.

Solutions in the Environment

Solutions are of utmost importance in the environment Figure 7.2). Solutions transport environmental chemical species in the aquatic environment and are crucial participants in geochemical processes. Dissolution in rainwater is the most common process by which atmospheric pollutants are removed from air. Acid rain is a solution of strong mineral acids in water. Many important environmental chemical processes occur in solution and at the interface of solutions with solids and gases.

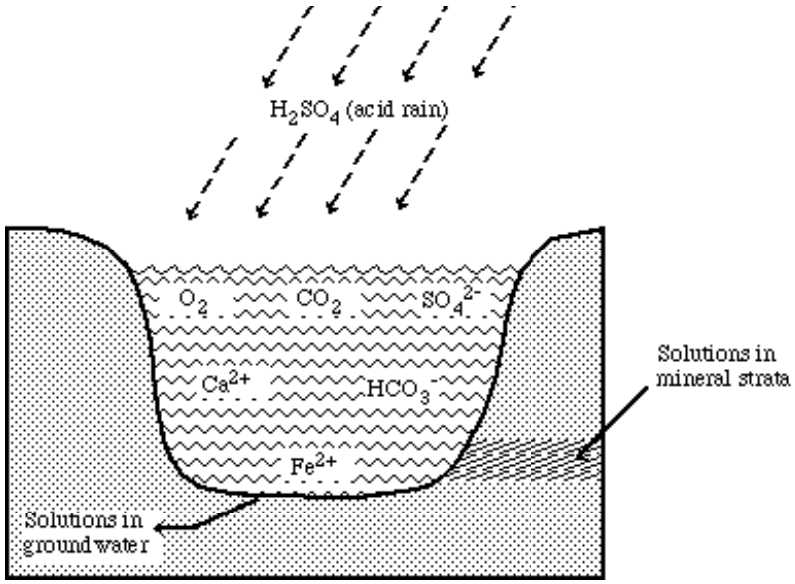


Figure 7.2 Many environmental chemical phenomena involve solutions.

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Pollutant pesticides and hazardous waste chemicals are transported in solution as surface water or groundwater. Many hazardous waste chemicals are dissolved in solution; often the large amount of water in which they are dissolved makes their treatment relatively more difficult and expensive.

Industrial Uses of Solutions

Solutions are used throughout industry. Many chemical reactions that are part of the manufacture of important industrial chemicals occur in solutions, and the chemical processes that take place in solution—**solution chemistry**—are very important in the chemical industry. *Natural brines* are solutions that contain a lot of dissolved materials and that occur underground and in some lakes (saline lakes). Some natural brines are important sources of valuable chemicals. Commercially important chemicals that are recovered from brines include borax, a compound containing boron and oxygen, which is used as an antiseptic, in making ceramics, and in some cleaning formulations; bromine salts; and potassium salts, including those used in potassium fertilizer. Solutions of detergents are used for cleaning; some dyes are applied as solutions. Ammonia fertilizer may be added to the soil as a solution of NH_3 in water.

Many organic materials do not dissolve significantly in water. Such substances are usually soluble in organic solvents, such as benzene and carbon tetrachloride. When used to dissolve organic substances, organic liquids are commonly called solvents. Some aspects of solvents are discussed in the following section.

7.2 SOLVENTS

Water is the solvent for most of the solutions discussed in this chapter. However, as noted above, many other liquids are also used as solvents. Other than water, most solvents are organic (carbon-containing) liquids. Some of the more important organic solvents are shown in Table 7.1.

There are many uses for solvents. One of the most important of these is their role as media in which chemical reactions may occur. In the chemical industry, solvents are employed for purification, separation, and physical processing. Solvents are also used for cleaners; one important example is the use of organic solvents to dissolve grease and oil from metal parts after they have been fabricated. (In the past, though less so now, solvents used for parts cleaning were allowed to evaporate to the atmosphere, a major source of atmospheric organic pollutants.) The chemicals that make up synthetic fibers, such as rayon, are dissolved in solvents, then forced under very high pressure through small holes in a special die to make individual filaments of the fiber. One of the most important uses for solvents is in coatings, which include paint, printing inks, lacquers, and antirust formulations. In order to apply these coatings, it is necessary to dissolve them in a solvent (**vehicle**) so that they may be spread around on the surface to be coated. The vehicle is a **volatile** liquid, one that evaporates quickly to form a vapor; when it evaporates, it leaves the coating behind as a thin layer.

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Fire and toxicity are major hazards associated with the use of many solvents. Some organic solvents, such as benzene, are even more of a fire hazard than gasoline. Both benzene and carbon tetrachloride are toxic and can damage the body in cases of excess exposure. Benzene is suspected of causing leukemia, and worker exposure to this solvent is now carefully regulated. The toxicity hazard of solvents arises from absorption through the skin and inhalation through the lungs. One solvent, dimethyl sulfoxide, is relatively harmless by itself but has the property of carrying toxic solutes through the skin and into the body. Exposure to solvent vapor is limited by occupational health regulations which include a threshold limiting value (TLV). This is the measure of solvent vapor concentration in the atmosphere considered safe for exposure to healthy humans over a normal 40-hour work week.

Table 7.1 Important Organic Solvents

Solvent	Solvent Use (may have many other nonsolvent uses)	Approximate Annual U.S. Production, millions of kilograms
Acetone	Solvent for spinning cellulose acetate fibers and for spreading paints and other protective coatings.	1,000
Benzene	Dissolves grease and other organic compounds.	6,500
Perchloroethylene	Best solvent for dry cleaning, also used for degreasing metals and extraction of fats.	125
Stoddard solvent	Mixture of alkanes and aromatic hydrocarbons containing from 7 to 12 C atoms per molecule used as a solvent for organic materials	17
Toluene	Dissolves grease and other organic materials; substitute for benzene, but not so toxic	2,700
Trichloroethylene	Vapor degreasing of metal parts; solvent for greases, oils, fats, waxes, and tars; fabric cleaner; waterless dying; ingredient of formulations of adhesives, lubricants, paints, varnishes, paint strippers	90

7.3 WATER—A UNIQUE SOLVENT

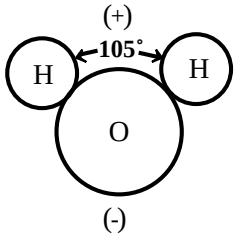
The remainder of this chapter deals with water as a solvent. Water is such an important compound that all of Chapter 11 is spent discussing it in detail. Here, just those properties of water that relate directly to its characteristics as a solvent are summarized.

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At room temperature H_2O is a colorless, tasteless, odorless liquid. It boils at 100°C (212°F) and freezes at 0°C (32°F). Water by itself is a very stable compound; it is very difficult to break up by heating. However, as explained in Section 8.6, when electrically conducting ions are present in water, a current may be passed through the water, causing it to break up into hydrogen gas and oxygen gas.

Water is an excellent solvent for a variety of materials; these include many ionic compounds (acids, bases, salts). Some gases dissolve well in water, particularly those that react with it chemically. Sugars and many other biologically important compounds are also soluble in water. However, greases and oils generally are not soluble in water but dissolve in organic solvents instead.

Some of water's solvent properties can best be understood by considering the structure and bonding of the water molecule:



The water molecule is made up of two hydrogen atoms bonded to an oxygen atom. The three atoms are not in a straight line, but form an angle of 105°.

Because of water's bent structure and the fact that the oxygen atom attracts the negative electrons more strongly than do the hydrogen atoms, the water molecule behaves like a body having opposite electrical charges at either end or pole. Such a body is called a *dipole*. Due to the fact that it has opposite charges at opposite ends, the water dipole may be attracted to either positively or negatively charged ions. Recall that NaCl dissolves in water to form positive Na^+ ions and negative Cl^- ions in solution. The positive sodium ions are surrounded by water molecules with their negative ends pointed at the ions, and the chloride ions are surrounded by water molecules with their positive ends pointing at the negative ions, as shown in Figure 7.3. This kind of attraction for ions is the reason why water dissolves many ionic compounds and salts that do not dissolve in other liquids. Some noteworthy examples are sodium chloride in the ocean; waste salts in urine; calcium bicarbonate, which is very important in lakes and in geological processes; and widely used industrial acids (such as HNO_3, HCl, and H_2SO_4).

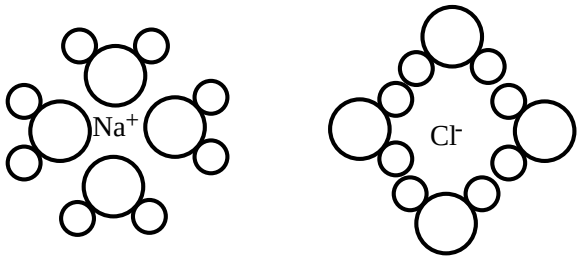


Figure 7.3 Polar water molecules surrounding Na^+ ion (left) and Cl^- ion (right).

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In addition to being a polar molecule, the water molecule has another important property which gives it many of its special characteristics: the ability to form **hydrogen bonds**. Hydrogen bonds are a special type of bond that can form between the hydrogen in one water molecule and the oxygen in another water molecule. This bonding takes place because the oxygen has a partly negative charge and the hydrogen, a partly positive charge. Hydrogen bonds, shown in Figure 7.4 as dashed lines, hold the water molecules together in large groups.

Hydrogen bonds also help to hold some solute molecules or ions in solution. This happens when hydrogen bonds form between the water molecules and hydrogen or oxygen atoms on the solute molecule (see Figure 7.4). Hydrogen bonding is one of the main reasons that some proteins can be put in water solution or held suspended in water as extremely small particles called *colloidal particles* (see Section 7.9).

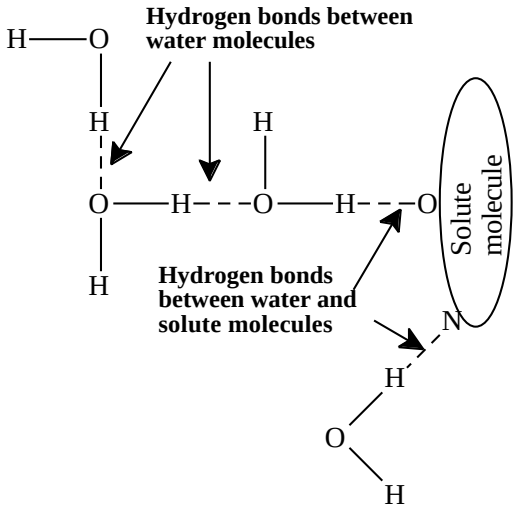


Figure 7.4 Hydrogen bonding between water molecules and between water molecules and a solute molecule in solution.

7.4 THE SOLUTION PROCESS AND SOLUBILITY

Very little happens to simple molecules, such as N_2 and O_2, when they dissolve in water. They mingle with the water molecules and occupy spaces that open up between water molecules to accomodate the N_2 and O_2 molecules. If the water is heated, some of the gases are driven out of solution. This may be observed as the small bubbles that appear in heated water just before it boils. A fish can extract some of the oxygen in water by "breathing" through its gills; just 6 or 7 parts of oxygen in a million parts of water is all that fish require. Water saturated with air at 25°C contains about 8 parts per million oxygen. Chapter 12 discusses how only a small amount of an oxygen-consuming substance can use up this tiny portion of oxygen in water and cause the fish to suffocate and die.

Although N_2 and O_2 dissolve in water in the simple form of their molecules, the situation is much different when hydrogen chloride gas, HCl, dissolves in water. The hydrogen chloride molecule consists of a hydrogen atom bonded to a chlorine atom

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with a covalent bond. (Recall that covalent bonds are formed by *sharing* electrons between atoms.) Water can absorb large amounts of hydrogen chloride: 100 grams of water at 0°C will dissolve 82 g of this gas. When HCl dissolves in water (Figure 7.5), the solution is not simply hydrogen chloride molecules mixed with water molecules. The water has a strong effect upon the HCl molecule, breaking it into two parts, with the 2 electrons in the chemical bond staying with the chlorine. This forms a positively charged hydrogen ion, H^+, and a negatively charged chloride ion, Cl^-.

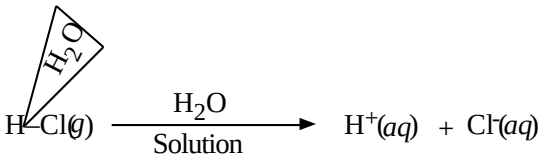


Figure 7.5 HCl dissolving in water. Water breaks apart a hydrogen chloride molecule to form a hydrogen ion, H^+, and a chloride ion, Cl^-.

In water solution, the chloride ion is surrounded by the positive ends of the water molecules, which are attracted to the negatively charged Cl^- ion. This kind of attraction of water molecules for a negative ion has already been shown in Figure 7.3. The H^+ ion from the HCl molecule does not remain in water as an isolated ion; it attaches to an unshared electron pair on a water molecule. This water molecule, with its extra hydrogen ion and extra positive charge, becomes a different ion with a formula of H_3O^+; it is called a **hydronium ion**. Although a hydrogen ion in solution is indicated as H^+ for simplicity, it is really present as part of a hydronium ion or larger ion aggregates ($H_5O_2^+$, $H_7O_3^+$).

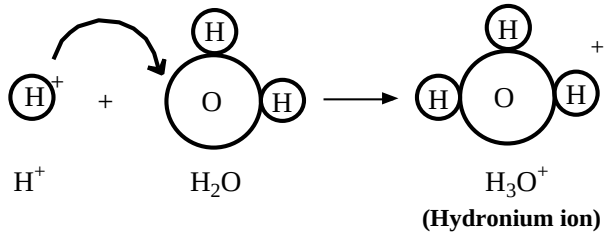


Figure 7.6 A hydrogen ion, H^+, bonds to a water molecule, H_2O, to produce a hydronium ion, H_3O^+. Bonding to additional water molecules may form larger aggregates, $H_5O_2^+$, $H_7O_3^+$.

The solution of hydrogen chloride in water illustrates a case in which a neutral molecule dissolves and forms electrically charged ions in water. While this happens with other substances dissolved in water, the hydrogen ion resulting when substances like HCl dissolve in water is particularly important because it results in the formation of a solution of acid. So rather than calling this a solution of hydrogen chloride, it is called a **hydrochloric acid** solution.

7.5 SOLUTION CONCENTRATIONS

In describing a solution it is necessary to do so *qualitatively*, that is, to specify what the solvent is and what the solutes are. For example, it was just seen that HCl gas is the solute placed in water to form hydrochloric acid. It is also necessary to

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know what happens to the material when it dissolves. For instance, one needs to know that hydrogen chloride molecules dissolved in water form H^+ ions and Cl^- ions. In many cases it is necessary to have *quantitative* information about a solution, its **concentration**. The concentration of a solution is the *amount* of solute material dissolved in a particular amount of solution, or by a particular amount of solvent. Solution concentration may be expressed in a number of different ways. Solutions used in technical applications, such as for cleaning, are often made up of a specified number of grams of solute per 100 mL (milliliters) of solvent added. On the other hand, a person involved in crop spraying may mix the required solution by adding several pounds of pesticide to a specified number of barrels of water.

The concentrations of water pollutants frequently are given in units of milligrams per liter (mg/L). Most of the chemicals that commonly pollute water are harmful at such low levels that milligrams per liter of water is the most convenient way of expressing their concentrations. For example, water containing more than about one-third of a milligram of iron per liter of water can stain clothing and bathroom fixtures. To get an idea of how small this quantity is, consider that a liter of water (strictly speaking, at 4˚C) weighs 1 million milligrams. Water containing one-third part per million of iron contains only 1 mg of iron in 3 million milligrams (3 liters) of water. Because 1 liter of water weighs 1 million milligrams, 1 mg of a solute dissolved in a liter is a **part per million**, abbreviated as **ppm**. The terms *part per million* and *milligrams per liter* are both frequently used in reference to levels of pollutants in water.

Some pollutants are so poisonous that their concentrations are given in micrograms per liter (μg/liter). A particle weighing a microgram is so small that it cannot be seen with the naked eye. Since a microgram is a millionth of a gram, a liter of water weighs 1 billion micrograms. So, 1 microgram per liter is **1 part per billion (ppb)**. Sometimes it is necessary to think in terms of concentrations that are this low; a good example of this involves the long-banned pesticide *Endrin*. It is so toxic that, at a concentration of only two-thirds of a microgram per liter, it can kill half of the fingerlings (young fish) in a body of water over a four-day period.

At the other end of the scale, it may be necessary to consider very high concentration; these are often given as *percent by weight.* As indicated in Figure 7.7, the concentrations of commercial acids and bases are often expressed in this way. For example, a solution of concentrated ammonia purchased for laboratory use is *28% by mass* NH_3; this means that out of 100 g of the ammonia solution, 28 g are NH_3 and 72 g are water. Commercial hydrochloric acid is about 36% by mass hydrogen chloride, HCl: of 100 g of concentrated hydrochloric acid, 36 g are HCl and 64 g are water.

Molar Concentration

The *mass* of a solute in solution often does not provide full information about its effect. For example, a solution of either NaCl or sodium iodide (NaI) will remove silver from a solution of silver nitrate ($AgNO_3$) when the two solutions are mixed. The two possible chemical reactions are,

$$AgNO_3(aq) + NaCl(aq) \rightarrow NaNO_3(aq) + AgCl(s) \qquad (7.5.1)$$

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$$AgNO_3(aq) + NaI(aq) \rightarrow NaNO_3(aq) + AgI(s) \quad (7.5.2)$$

in which solid precipitates of AgCl and AgI, respectively, come out of solution. The molcular mass of NaCl is 58.5 and that of NaI is 149.9. By comparing the removal of silver from solution by solutions of NaCl and NaI, both containing the same mass of solid in a specific volume of solution, it can be seen that a given volume of NaCl solution removes more silver. In chemical reactions such as these, it is the number of ions or molecules that is important, not their masses in solution. It would be convenient to have a way of expressing concentrations in quantities that would be directly

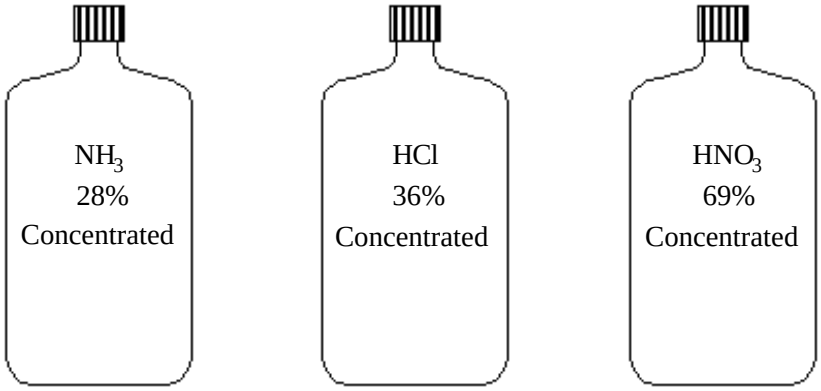


Figure 7.7 Percentages of solutes in commercial solutions of ammonia, hydrochloric acid, and nitric acid.

related to the number of molecules or ions in solution. Instead of expressing such huge numbers, however, the chemist normally works with *moles*. (Recall from Section 2.3 that a mole is the number of grams of a substance that is equal numerically to the mass in amu of the smallest unit of the substance. For example, since the molecular mass of NaCl is 58.5, a mole of NaCl weighs 58.5 g.) The **molar concentration** of a solution is *the number of moles of solute dissolved in a liter of solution*. Molar concentration is abbreviated with the letter M. A 1 M solution has 1 mole of solute dissolved in a liter of solution. To understand this concept better, consider the following:

- The molecular mass of HCl is 36.5; a 1 M solution of HCl has 1 mole of HCl (36.5 g) dissolved in a liter of solution.
- The molecular mass of NH_3 is 17; a 1 M solution of NH_3 has one mole of NH_3 (17 g) in a liter of solution.
- The molecular mass of glucose, $C_6H_{12}O_6$, is 180; a 1 M solution of glucose has 1 mole of glucose (180 g) in a liter of solution.

Of course, solutions are not always exactly 1 M in concentration. However, it is easy to perform calculations involving molar concentration using the relationships expressed in the following equation:

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$$M = \frac{\text{Moles solute}}{\text{Volume solution, L}} = \frac{\text{Mass solute, g}}{\text{Molar mass solute} \times \text{Volume solution, L}} \quad (7.5.3)$$

To see how this equation can be used, consider the following examples:

Example: What is the molar concentration of a solution that contains 2.00 moles of HCl in 0.500 L of solution?

Answer:

$$M = \frac{2.00 \text{ mol}}{0.500 \text{ L}} = 4.00 \text{ mol/L}$$

Example: What is the mass of HCl, molar mass 36.5 g/mol in 2.75 L of a 0.800 M solution?

Answer:

$$0.800 \text{ mol/L} = \frac{\text{Mass solute}}{36.5 \text{ g/mol} \times 2.75 \text{ L}}$$

Mass solute = 0.800 mol/L x 36.5 g/mol x 2.75 L = 80.3 g

$$M = \frac{\text{Mass solute, g}}{\text{Molar mass solute} \times \text{Volume solution, L}}$$

Example: What is the molar concentration of a solution containing 87.6 g of HCl in a total volume of 3.81 L of solution?

Answer:

$$M = \frac{87.6 \text{ g}}{36.5 \text{ g/mol} \times 3.81 \text{ L}} = 0.630 \text{ mol/L}$$

To summarize the steps involved in making up a certain quantity of a solution with a specified concentration, consider the task of making up 4.60 liters of 0.750 M NaCl, which would involve the following steps:

Step 1. Calculate the mass of NaCl, molar mass 58.5 g/mol, required.

$$0.750 \text{ mol/L} = \frac{\text{Mass solute}}{58.5 \text{ g/mol} \times 4.60 \text{ L}}$$

Mass solute = 0.750 mol/L × 58.5 g/mol × 4.60 L = 202 g

Step 2. Weigh out 202 g NaCl

Step 3. Add NaCl to a container with a mark at 4.60 L

Step 4. Add water and mix to a final volume of 4.60 L

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Diluting Solutions

Often it is necessary to make a less concentrated solution from a more concentrated solution; this process is called **dilution**. This situation usually occurs in the laboratory because it is more convenient to store more-concentrated solutions in order to save shelf space. Also, laboratory acid solutions, such as those of hydrochloric acid, sulfuric acid, and phosphoric acid, are almost always purchased as highly concentrated solutions; these are more economical because there is more of the active ingredient per bottle. For standard solutions to use in chemical analysis, it is more accurate to weigh out a relatively large quantity of solute to make a relatively concentrated solution, then dilute the solution quantitatively to prepare a more dilute standard solution.

For example, the concentration of commercial concentrated hydrochloric acid is 12 M. A laboratory technician needs 1 liter of 1 M hydrochloric acid. How much of the concentrated acid is required? The key to this problem is to realize that when a volume of the concentrated acid is diluted with water, the total *amount of solute acid* in the solution remains the same. The problem can then be solved by considering the equation

$$M = \frac{\text{Moles solute}}{\text{Volume solution}} \tag{7.5.3}$$

using subscripts "1" and "2" to indicate values before and after dilution, respectively,

$$M_1 = \frac{(\text{Moles solute})_1}{(\text{Volume solution})_1} \tag{7.5.4}$$

$$M_2 = \frac{(\text{Moles solute})_2}{(\text{Volume solution})_2} \tag{7.5.5}$$

and setting "Moles solute" before and after dilution equal to each other:

$$M_1 \times (\text{Volume solution})_1 = M_2 \times (\text{Volume solution})_2 \tag{7.5.6}$$

In the example cited above, the volume of HCl before dilution is to be calculated:

$$(\text{Volume solution})_1 = \frac{M_2 \times (\text{Volume solution})_2}{M_1} \tag{7.5.7}$$

$$(\text{Volume solution})_1 = \frac{1\ \text{Mol/L} \times 1\ \text{L}}{12\ \text{mol/L}} = 0.083\ \text{L} \tag{7.5.8}$$

The result of this calculation shows that 0.083 L, or 83 mL of 12 M HCl must be taken to make 1.00 L of 12 M solution.

The same general approach used in solving these dilution problems can be used when concentrations are expressed in units other than molar concentration. Concentrations of metals dissolved in water are frequently measured by *atomic absorption*

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spectroscopy, a technique discussed in Chapter 25. To measure the concentration of metal in an unknown solution, it is necessary to have a standard solution (see Section 7.6) of known concentration. As purchased, these standard solutions contain 1000 mg of the desired metal dissolved in 1 liter of solution. Suppose one had a standard solution of $CaCl_2$ containing 1000 mg of Ca^{2+} per liter of solution. How would this solution be diluted to make 5 liters of a solution containing 20 mg of calcium per liter?

Step 1. Consider how many milligrams of calcium are in the desired 5 L of solution containing 20 mg of calcium per liter.

$$5\ \text{L} \times 20\ \text{mg calcium/L} = 100\ \text{mg calcium} \qquad (7.5.9)$$

Step 2. Find how much standard solution containing 1000 mg of calcium per liter contains 100 mg of calcium.

$$\frac{100\ \text{mg of calcium}}{1000\ \text{mg calcium/L}} = 0.100\ \text{L of standard solution} \qquad (7.5.10)$$

Step 3. Dilute 0.100 L (100 mL) of the standard calcium solution to 5 L to obtain the desired solution containing 20 mg of calcium per liter.

Molar Concentration of H^+ Ion and pH

Concentrations are important in expressing the degree to which solutions are acidic or basic. Recall that **acids**, such as HCl and H_2SO_4, produce H^+ ion, whereas **bases**, such as sodium hydroxide and calcium hydroxide (NaOH and $Ca(OH)_2$, respectively), produce hydroxide ion, OH^-. Molar concentrations of hydrogen ion, $[H^+]$, range over many orders of magnitude and are conveniently expressed by pH defined as

$$\text{pH} = -\log[H^+] \qquad (7.5.11)$$

In absolutely pure water the value of $[H^+]$ is exactly 1×10^{-7} mole/L, the pH is 7.00, and the solution is **neutral** (neither acidic nor basic). **Acidic** solutions have pH values of less than 7 and **basic** solutions have pH values of greater than 7.

Solubility

If a chemist were to attempt to make a solution containing calcium ion by dissolving calcium carbonate, $CaCO_3$ in water, not much of anything would happen. The chemist would not observe any calcium carbonate dissolving, because its **solubility** in water is very low. Only about 5 mg (just a small white "speck") of calcium carbonate will dissolve in a liter of water.

This illustrates an important point that people working in laboratories should keep in mind. When preparing a solution, it is a good idea to look up the solubility of the compound being dissolved. Make sure that the solubility is high enough to give

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the concentration that is desired. Many futile hours have been spent shaking bottles, trying to get something to dissolve whose solubility is just too low to make the desired solution.

A solution that has dissolved as much of a solute as possible is said to be **saturated** with regard to that solute. The *concentration* of the substance in the *saturated* solution is the **solubility.** Solubilities of different substances in water vary enormously. At the low end of the scale, even glass will dissolve a little bit in water, although the concentration of glass in solution is very, very low. Even this very small solubility can cause difficulties in the analysis of silicon (one of the elements in glass). This is because the dissolved glass increases the silicon content of the water in the solution, which throws off the results of the analysis. Antifreeze (composed of an organic compound called *ethylene glycol*) is an example of a substance that is completely soluble in water. One could pour a cup of water into a barrel and keep adding antifreeze without ever getting a saturated solution of antifreeze in water, even if the barrel were filled to the point of overflowing.

Supersaturated Solutions

Consider what happens when a bottle of carbonated beverage at an elevated temperature is opened. As the cap comes off, there is a loud pop, and the contents pour forth in a geyser of foam. This is because the solution of CO_2 in the bottle is a **supersaturated** solution. The carbon dioxide is added to the cold beverage under pressure. When the contents of the bottle become warm and the pressure is released by removing the bottle cap, the solution suddenly contains more CO_2 than it can hold in an unpressurized solution. This is because as CO_2 becomes warmer, its solubility decreases.

Factors Affecting Solubility

Solubility is affected by several factors. The preceding example has shown two of the most important factors affecting *gas* solubility: temperature and pressure. The solubilities of gases such as CO_2 *decrease* with *increasing* temperature. A gas is much less soluble in water just about hot enough to boil than it is in water just about cold enough to freeze. However, once the solution freezes, the gas is not at all soluble in the ice formed. This can be illustrated vividly with soft drinks, which also contain carbon dioxide dissolved under pressure. A can of soda placed in the freezer to cool quickly and then forgotten may burst from the pressure of the carbon dioxide coming out of solution as the liquid freezes, causing havoc in its immediate surroundings.

The solubilities of most solids *increase* with *rising* temperature, although not in all cases. Sugar, for example, is much easier to dissolve in a cup of hot tea than in a glass of iced tea.

One of the most important things affecting solubility is the presence of other chemicals in the solution that react with the solute. For example, CO_2 is really not very soluble in water. But, if the water already contains some NaOH (sodium hydroxide), the carbon dioxide is very soluble because a chemical reaction occurs between NaOH and CO_2 to form highly soluble sodium bicarbonate, $NaHCO_3$.

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$$NaOH + CO_2 \text{ (not very soluble)} \rightarrow NaHCO_3 \text{ (highly soluble)} \quad (7.5.12)$$

7.6 STANDARD SOLUTIONS AND TITRATIONS

Standard solutions are those of known concentration that are widely used in chemical analysis. Basically, a standard solution is one against which a solution of unknown concentration can be compared to determine the concentration of the latter. One of the most common and straightforward means of comparison is by way of **titration**, which consists of measuring the amount of a standard solution that reacts

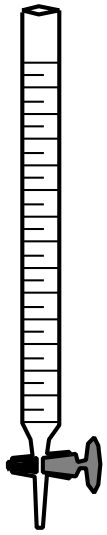


Figure 7.8 A buret, a long glass tube with marks on it and a stopcock on the end, is used to measure the volume of standard solution added to a sample during titration.

with a sample using the apparatus illustrated in Figure 7.8. As an example consider a hospital incinerator with a water scrubbing system to clean exhaust gases. Suppose it is observed that the scrub water contains hydrochloric acid from the burning of chlorine-containing plastics and that this acid is corroding iron drain pipes, a problem that can be eliminated by adding sodium hydroxide to neutralize the acid. The amount of base needed may be determined by *titration*, a procedure in which a measured volume of the hydrochloric acid-containing scrub solution is reacted with a standard solution of NaOH,

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O \quad (7.6.1)$$

until just enough base has been added to react with all the HCl in the measured volume of sample. The point at which this occurs is called the **end point** and is shown by an abrupt change in color of a dissolved dye called an **indicator**. Phenolphthalein, a dye that is red in base and colorless in acid is commonly used as an indicator.

Suppose that 50.0 mL (0.0500 L) of waste incinerator scrubber water were titrated with 0.0100 M standard NaOH, requiring 40.0 (0.0400 L) mL of the titrant solution. The molar concentration of the HCl in the sample can be calculated from

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an equation derived from the following:

$$M = \frac{\text{Moles solute}}{\text{Volume solution}} \tag{7.5.3}$$

In this case, as shown by Reaction 7.6.1, the number of moles of HCl in the sample exactly equals the number of moles of NaOH at the end point, which leads to the relationship

$$M_{HCl} \times \text{Volume HCl} = M_{NaOH} \times \text{Volume NaOH} \tag{7.6.2}$$

where the subscript formulas denote HCl and NaOH solutions. This equation can be rearranged and values substituted into it to give the following:

$$M_{HCl} = \frac{M_{NaOH} \times \text{Volume NaOH}}{\text{Volume HCl}} \tag{7.6.3}$$

$$M_{HCl} = \frac{0.0100 \text{ mol/L} \times 0.0400 \text{ L}}{0.0500 \text{ L}} = 0.00800 \text{ mol/L} \tag{7.6.4}$$

From this concentration, the quantity of base that must be added to neutralize the waste acid can be calculated.

7.7 PHYSICAL PROPERTIES OF SOLUTIONS

The presence of solutes in water can have profound effects upon the properties of the solvent. These effects include lowering the freezing point, elevating the boiling point, and osmosis. All such properties are called **colligative properties**; they depend upon the concentration of solute, rather than its particular identity. The effects of solutes and solution concentrations on colligative properties are addressed briefly here.

Freezing Point Depression

One of the most practical uses of solutions depends upon the effect that materials dissolved in water have upon the temperature at which the water, or the solution, freezes. Solutions freeze at lower temperatures than does water. This phenomenon is applied in the cooling systems of automobiles. Most automobile engines are water-cooled, that is, water circulates through the engine, picking up heat, and then goes to a radiator where the excess heat is given off. If pure water is left in an engine at freezing temperatures, it will, of course, freeze. When water freezes, it expands, so that the ice that is formed has a larger volume than the original liquid. This increase in volume produces enormous forces that can crack the stoutest engine block as if it were an eggshell.

To prevent an engine block from damage by freezing and expansion of the coolant, antifreeze is mixed with water in the cooling system. The chemical name of antifreeze is ethylene glycol, and it has the chemical formula $C_2H_6O_2$. A solution containing 40% ethylene glycol and 60% water by mass freezes at -8° Fahrenheit, or

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-22.2° Celsius. (Recall that pure water freezes at 32°F, or O°C; it boils at 212°F, or 100°C.) A solution containing exactly half ethylene glycol and half water by mass freezes at -29°F.

Boiling Point Elevation

Solutions can also keep water from boiling. For instance, mixing antifreeze or other materials that do not boil easily with water raises the boiling temperature. Because of the higher boiling temperature, a solution of antifreeze in water makes a good "summer coolant." In fact, antifreeze is now marketed as "antifreeze-antiboil" and is virtually required in an engine to keep the cooling system from boiling in summer's heat.

Osmosis

Human blood consists chiefly of red blood cells suspended in a fairly concentrated solution or **plasma**. The dissolved material making up the solution is mostly sodium chloride at around 0.15 molar concentration. The red blood cells also contain a solution much like the plasma in which they float. If one were to take some blood, force the red cells to settle out by spinning test tubes full of blood samples in a centrifuge and then place the red cells in pure water, a strange effect would be observed. When viewed under a microscope, the cells would be seen to swell and finally burst. This is an example of **osmosis**, the process whereby a substance passes through a membrane, from an area of higher concentration of the substance to an area of lower concentration of the substance. Water can go through the membrane that holds the red blood cell together. When the cell is placed in pure water, the water tends to pass through the membrane to the more concentrated salt solution inside the cell. One way of looking at it is to say that the solution inside the cell has relatively less water, so that water from the outside has a tendency to enter the cell. Finally, so much water gets in that it breaks the cell apart (Figure 7.9). However, when a blood cell is placed in a very strong solution of sodium chloride, the opposite effect is observed: water passes from inside the cell to the outside, where there is less water, relative to sodium chloride, and the cell shrivels up (Figure 7.10).

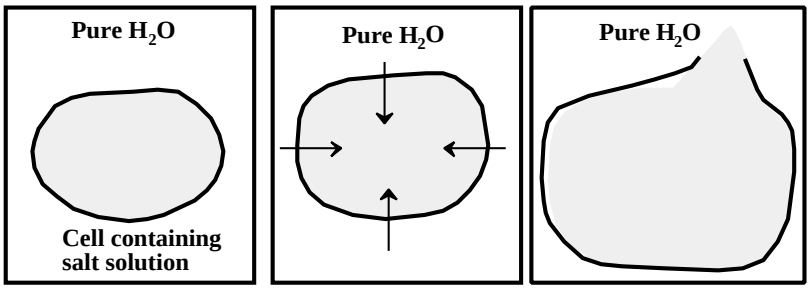


Figure 7.9 Osmosis causes pure water to be absorbed by a red blood cell, increasing the pressure in the cell and causing it to burst.

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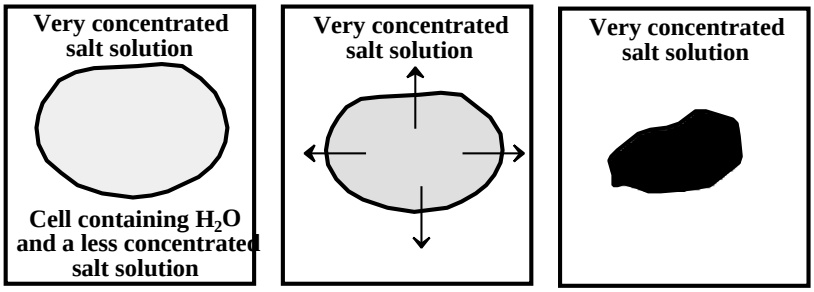


Figure 7.10 Osmosis causes water inside a red blood cell to pass out into a concentrated salt solution, causing the cell to shrivel.

Many biological membranes, such as the "wall" surrounding a red blood cell, allow material to pass through. Water in the ground tends to move through cell membranes in root cells and finally to plant leaves, where it evaporates to form water vapor in the atmosphere (a process called *transpiration*). Osmosis is a major part of the driving force behind these processes.

The concentration of a solution relative to another solution determines which solution water will have a tendency to enter. *Water* tends to enter a solution of higher concentration (of some other substance), since it contains *less water*, relatively speaking. This can be particularly important in blood. Solutions injected into the veins for feeding, or to replace body fluids lost due to illness, must be prepared so that they will not cause water to move into or out of the cells by osmosis. Such a solution, which prevents osmosis from taking place, is called an **isotonic** solution. It is sometimes referred to as a *physiological* solution. Its use prevents damage to blood cells by either shrinking or swelling.

Osmosis may result in the buildup of a very high pressure called **osmotic pressure**. It is this pressure that can get so high in a red blood cell suspended in water that the cell bursts. Osmotic pressure can be several times atmospheric pressure.

Pure water tends to move by osmosis through a membrane to a more "contaminated" solution. Application of sufficient opposite pressure can "squeeze" water out of a contaminated solution, producing pure water. This process is called **reverse osmosis**, and is commonly used to purify small quantities of water. Some very large reverse osmosis installations are now being used to remove salt from seawater, a process called **desalination**.

7.8 SOLUTION EQUILIBRIA

Solution Equilibria

Many phenomena in aquatic chemistry and geochemistry involve **solution equilibrium**. In a general sense solution equilibrium deals with the extent to which **reversible** acid-base, solubilization (precipitation), complexation, or oxidation-reduction reactions proceed in a forward or backward direction. This is expressed for a generalized equilibrium reaction,

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$$aA + bB \leftrightarrow cC + dD \tag{7.8.1}$$

by the following **equilibrium constant expression**:

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = K \tag{7.8.2}$$

where K is the **equilibrium constant**.

A reversible reaction may approach equilibrium from either direction. In the example above, if A were mixed with B, or C were mixed with D, the reaction would proceed in a forward or reverse direction such that the concentrations of species—[A], [B], [C], and [D]—substituted into the equilibrium expression gave a value equal to K.

As expressed by **Le Châtelier's principle**, a stress placed upon a system in equilibrium will shift the equilibrium to relieve the stress. For example, adding product "D" to a system in equilibrium will cause Reaction 7.8.1 to shift to the left, consuming "C" and producing "A" and "B," until the equilibrium constant expression is again satisfied. This is called the **mass action effect**, and it is the driving force behind many environmental chemical phenomena.

There are several major kinds of equilibria in aqueous solution. One of these is **acid–base equilibrium** as exemplified by the ionization of acetic acid, HAc,

$$HAc \leftrightarrow H^+ + Ac^- \tag{7.8.3}$$

for which the acid dissociation constant is K_a:

$$\frac{[H^+][Ac^-]}{[HAc]} = K_a = 1.75 \times 10^{-5} \quad (\text{at } 25^\circ C) \tag{7.8.4}$$

Very similar expressions are obtained for the formation and dissociation of metal **complexes** or **complex ions**, formed by the reaction of a metal ion in solution with a **complexing agent** or **ligand**, both of which are capable of independent existence in solution. This can be shown by the reaction of iron(III) ion and thiocyanate ligand

$$Fe^{3+} + SCN^- \leftrightarrow FeSCN^{2+} \tag{7.8.5}$$

for which the **formation constant expression** is:

$$\frac{[FeSCN^{2+}]}{[Fe^{3+}][SCN^-]} = K_f = 1.07 \times 10^3 \quad (\text{at } 25^\circ C) \tag{7.8.6}$$

The bright red color of the $FeSCN^{2+}$ complex formed could be used to test for the presence of iron(III) in acid mine water.

An example of an **oxidation-reduction reaction** (those that involve the transfer of electrons between species) is

$$MnO_4^- + 5Fe^{2+} + 8H^+ \leftrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O \tag{7.8.7}$$

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for which the equilibrium expression is:

$$\frac{[Mn^{2+}][Fe^{3+}]^5}{[MnO_4^-][Fe^{2+}]^5[H^+]^8} = K = 3 \times 10^{62} \quad (\text{at } 25^\circ C) \tag{7.8.8}$$

The value of K is calculated from the Nernst equation (Chapter 8).

Distribution between Phases

Many important environmental chemical phenomena involve distribution of species between phases. This most commonly involves the equilibria between species in solution and in a solid phase. **Solubility equilibria** deal with reactions such as

$$AgCl(s) \rightarrow Ag^+ + Cl^- \tag{7.8.9}$$

in which one of the participants is a slightly soluble (virtually insoluble) salt and for which the equilibrium constant is K_{sp}.

$$[Ag^+][Cl^-] = K_{sp} = 1.82 \times 10^{-10} \quad (\text{at } 25^\circ C) \tag{7.8.10}$$

a **solubility product**. Note that in the equilibrium constant expression there is not a value given for the solid AgCl. This is because the activity of a solid (in this case the tendency of Ag^+ and Cl^- ions to break away from solid AgCl) is constant at a specific temperature and is contained in the value of K_{sp}.

An important example of distribution between phases is that of a hazardous waste species partitioned between water and a body of immiscible organic liquid in a hazardous waste site. The equilibrium for such a reaction

$$X(aq) \leftarrow \rightarrow X(org) \tag{7.8.11}$$

is described by the **distribution law** expressed by a **distribution coefficient** or **partition coefficient** in the following form:

$$\frac{[X(org)]}{[X(aq)]} = K_d \tag{7.8.12}$$

Solubilities of Gases

The solubilities of gases in water are described by Henry's Law, which states that *at constant temperature the solubility of a gas in a liquid is proportional to the partial pressure of the gas in contact with the liquid*. For a gas, "X," this law applies to equilibria of the type

$$X(g) \leftarrow \rightarrow X(aq) \tag{7.8.13}$$

and does not account for additional reactions of the gas species in water such as,

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$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \quad (7.8.14)$$

$$SO_2 + HCO_3^- \text{ (From water alkalinity)} \leftrightarrow CO_2 + HSO_3^- \quad (7.8.15)$$

which may result in much higher solubilities than predicted by Henry's Law alone.

Mathematically, Henry's Law is expressed as

$$[X(aq)] = K P_X \quad (7.8.16)$$

where $[X(aq)]$ is the aqueous concentration of the gas, P_X is the partial pressure of the gas, and K is the Henry's Law constant applicable to a particular gas at a specified temperature. For gas concentrations in units of moles per liter and gas pressures in atmospheres, the units of K are mol × L^{-1} × atm^{-1}. Some values of K for dissolved gases that are significant in water are given in Table 7.2.

Table 7.2 Henry's Law Constants for Some Gases in Water at 25˚C

Gas	K, mol × L^{-1} × atm^{-1}
O_2	1.28×10^{-3}
CO_2	3.38×10^{-2}
H_2	7.90×10^{-4}
CH_4	1.34×10^{-3}
N_2	6.48×10^{-4}
NO	2.0×10^{-4}

In calculating the solubility of a gas in water, a correction must be made for the partial pressure of water by subtracting it from the total pressure of the gas. At 25˚C, the partial pressure of water is 0.0313 atm; values at other temperatures are readily obtained from standard handbooks. The concentration of oxygen in water saturated with air at 1.00 atm and 25˚C can be calculated as an example of a simple gas solubility calculation. Considering that dry air is 20.95% by volume oxygen and factoring in the partial pressure of water gives the following:

$$P_{O_2} = (1.0000 \text{ atm} - 0.0313 \text{ atm}) \times 0.2095 = 0.2029 \text{ atm} \quad (7.8.17)$$

$$[O_2(aq)] = K \times P_{O_2} = 1.28 \times 10^{-3} \text{ mol} \times L^{-1} \times atm^{-1} \times 0.2029 \text{ atm}$$

$$= 2.60 \times 10^{-4} \text{ mol} \times L^{-1} \quad (7.8.18)$$

Since the molecular mass of oxygen is 32, the concentration of dissolved oxygen in water in equilibrium with air under the conditions given above is 8.32 mg/L, or 8.32 parts per million (ppm).

The solubilities of gases decrease with increasing temperature. Account is taken of this factor with the **Clausius-Clapeyron** equation,

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$$\log \frac{C_2}{C_1} = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad (7.8.19)$$

where C_1 and C_2 are the gas concentrations in water at absolute temperatures of T_1 and T_2, respectively, ΔH is the heat of solution, and R is the gas constant. The value of R is 1.987 $cal \times deg^{-1} \times mol^{-1}$, giving ΔH in units of cal/mol. Detailed calculations involving the Clausius-Clapeyron equation are beyond the scope of this chapter.

7.9 COLLOIDAL SUSPENSIONS

If some fine sand is poured into a bottle of water and shaken vigorously, the sand will float around in the water for a very brief time, then rapidly settle to the bottom. Particles like sand, which float briefly in water and then rapidly settle out, are called **suspensions**. It has already been seen that molecules or ions that dissolve in water and mingle individually with the water molecules make up *solutions*. Between these two extremes are particles that are much smaller than can be seen with the naked eye, but much larger than individual molecules. Such particles are called **colloidal particles**. They play important roles in living systems, transformations of minerals, and a number of industrial processes. Colloidal particles in water form **colloidal suspensions**. Unlike sand stirred in a jar, or soil granules carried by a vigorously running stream, *colloidal particles do not settle out of colloidal suspension by gravity alone*. Colloidal particles range in diameter from about 0.001 micrometer (μm) to about 1 μm, have some characteristics of both species in solution and larger particles in suspension, and in general exhibit unique properties and behavior. An important characteristic of colloidal particles is their ability to scatter light. Such light scattering is called the **Tyndall effect** and is observed as a light blue hue at right angles to incident white light. This phenomenon results from colloidal particles being the same order of size as the wavelength of light.

Individual cells of bacteria are colloidal particles and can form colloidal suspensions in water. Many of the green algae in water are present as colloidal suspensions of individual cells of the algae. Milk, mayonnaise, and paint are all colloidal suspensions. Colloids are used in making rubber, glue, plastics, and grease. The formation of a colloidal suspension of butterfat in milk is the process by which milk is *homogenized*, so that the cream does not rise to the top.

Kinds of Colloidal Particles

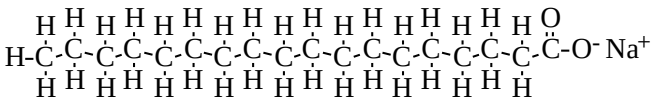
Colloids can be classified as *hydrophilic colloids*, *hydrophobic colloids*, or *association colloids*. These three classes are briefly summarized below.

Hydrophilic colloids generally consist of macromolecules, such as proteins and synthetic polymers, that are characterized by strong interaction with water resulting in spontaneous formation of colloids when they are placed in water. In a sense, hydrophilic colloids are solutions of very large molecules or ions. Suspensions of hydrophilic colloids are less affected by the addition of salts to water than are suspensions of hydrophobic colloids.

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Hydrophobic colloids interact to a lesser extent with water and are stable because of their positive or negative electrical charges as shown in Figure 7.11. The charged surface of the colloidal particle and the **counter-ions** that surround it compose an **electrical double layer**, which causes the particles to repel each other. Hydrophobic colloids are usually caused to settle from suspension by the addition of salts. Examples of hydrophobic colloids are clay particles, petroleum droplets, and very small gold particles.

Association colloids consist of special aggregates of ions and molecules called **micelles**. To understand how this occurs, consider sodium stearate, a typical soap with the structural formula shown below:



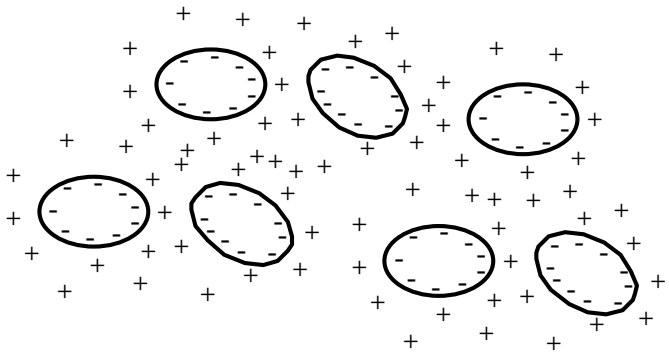


Figure 7.11 Representation of negatively charged hydrophobic colloidal particles surrounded in solution by positively charged counter-ions, forming an electrical double layer. (Colloidal particles suspended in water can have either a negative or positive charge.)

The stearate ion has both a hydrophilic $-CO_2^-$ head and a long organophilic $CH_3(CH_2)_{16}-$ tail. As a result, stearate anions in water tend to form clusters consisting of as many as 100 anions clustered together with their hydrocarbon "tails" on the inside of a spherical colloidal particle and their ionic "heads" on the surface in contact with water and with Na^+ counterions. This results in the formation of **micelles**, as illustrated in Figure 7.12.

Colloid Stability

The stability of colloids is a prime consideration in determining their behavior. It is involved in important aquatic chemical phenomena including the formation of sediments, dispersion and agglomeration of bacterial cells, and dispersion and removal of pollutants (such as crude oil from an oil spill).

Discussed above, the two main phenomena contributing to the stabilization of colloids are **hydration** and **surface charge**. The layer of water on the surface of hydrated colloidal particles prevents contact, which would result in the formation of larger units. A surface charge on colloidal particles may prevent aggregation, since like-charged particles repel each other. The surface charge is frequently pH-

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dependent; around pH 7 most colloidal particles in natural waters are negatively charged. Negatively charged aquatic colloids include algal cells, bacterial cells, proteins, and colloidal petroleum droplets.

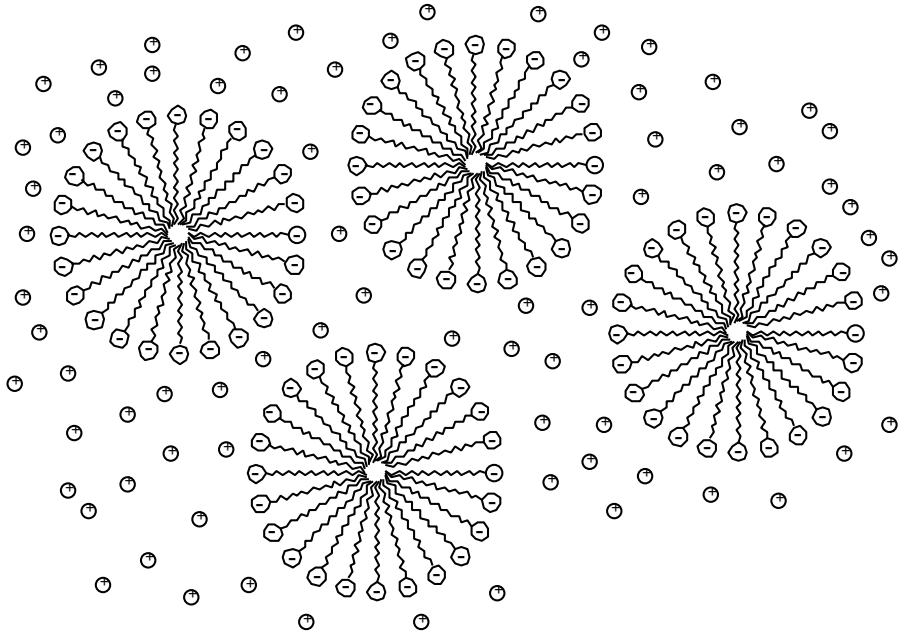


Figure 7.12 Representation of colloidal soap micelle particles. The stearate ions are shown as the following:

One of the three major ways in which a particle can acquire a surface charge is by **chemical reaction at the particle surface**. This phenomenon, which frequently involves hydrogen ion and is pH-dependent, is typical of hydroxides and oxides. As an illustration of pH-dependent charge on colloidal particle surfaces consider the effects of pH on the surface charge of hydrated manganese oxide, $MnO_2(H_2O)(s)$. In a relatively acidic medium, the reaction

$$MnO_2(H_2O)(s) + H^+ \rightarrow MnO_2(H_3O)^+(s) \qquad (7.9.1)$$

may occur on the surface giving the particle a net positive charge. In a more basic medium, hydrogen ion may be lost from the hydrated oxide surface to yield negatively charged particles:

$$MnO_2(H_2O)(s) \rightarrow MnO_2(OH)^-(s) + H^+ \qquad (7.9.2)$$

Ion absorption is a second way in which colloidal particles become charged. This phenomenon involves attachment of ions onto the colloidal particle surface by means other than conventional covalent bonding, including hydrogen bonding and London (Van der Waal) interactions.

Ion replacement is a third way in which a colloidal particle can gain a net charge. For example, replacement of some of the Si(IV) with Al(III) in the basic SiO_2 chemical unit in the crystalline lattice of some clay minerals,

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$$[SiO_2] + Al(III) \rightarrow [AlO_2^-] + Si(IV) \quad (7.9.3)$$

yields sites with a net negative charge. Similarly, replacement of Al(III) by a divalent metal ion such as Mg(II) in the clay crystalline lattice produces a net negative charge.

Coagulation and Flocculation of Colloidal Particles

The **aggregation** of colloidal particles is very important in a number of processes, including industrial processes and aquatic chemical phenomena. The ways in which colloidal particles of minerals come together and settle out of water are crucial in the formation of mineral deposits. The bacteria in colloidal suspension that devour sewage in the water at a sewage treatment plant must eventually be brought out of colloidal suspension to obtain purified water. Crude oil frequently comes out of the ground as a colloidal suspension in water; the colloidal particles of hydrocarbon must be separated from the water before the crude oil can be refined.

It is possible to force electrically charged colloidal particles to clump together and settle. This is done by adding charged ions, such as Na^+ and Cl^- ions, from sodium chloride. These charged ions tend to neutralize the electrical charges on the colloidal particles and allow them to come together; this process is called **coagulation**. In some cases, colloidal particles are caused to settle by virtue of *bridging groups* called *flocculants* that join the particles together. This phenomenon is called **flocculation**.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

A solid that seems to disappear when stirred with water is said to [1]_____, forming a [2]_____. The substance that dissolves is called the [3]_____, and the liquid in which it dissolves is the [4]_____. A substance that does not dissolve appreciably in a solvent is said to be [5]_____. Three typical organic solvents are [6]_____, _____, and _____. Two characteristics of water molecules that make water an excellent solvent for many substances are [7]_____ and _____. When O_2 dissolves in water, the oxygen molecules are in solution as [8]_____ _____. When NaCl dissolves in water it is present as [9]_____ _____, and when HCl dissolves in water it forms [10]_____. The hydrogen ion in water is bonded to a water molecule to form a [11]_____. The amount of solute in a particular amount of solution or solvent is the [12]_____ _____. Low concentrations of pollutants in water are often expressed as parts per [13]_____, abbreviated [14]_____, or, at even lower concentrations, as [15]_____, abbreviated [16]_____. The molar concentration of a solution is the number of [17]_____ of solute per [18]_____

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_____. The molecular mass of NH_3 is [19]_____, so a mole of ammonia weighs [20]_____. The molar concentration of a solution prepared by dissolving 8.5 g of NH_3 gas in 2 liters of solution is [21]_____ M. The relationships among the volume of a solution taken for dilution (V_1), its molar concentration (M_1), the volume of the diluted solution (V_2), and the concentration of the diluted solution (M_2) is [22]_____. The volume of 2 M HCl that must be diluted with water to make 5 liters of 1.5 M HCl is [23]_____ liters. The equation that defines pH is [24]_____. A pH less than 7 indicates a solution that is [25]_____. The maximum amount of solute that can dissolve in a particular volume of solution is called the solute's [26]_____. A solution containing the maximum amount of solute that it can normally hold is said to be [27]_____. A solution of known concentration used in chemical analyses is called a [28] _____. An operation in which the quantity of such a solution required to react with a substance in another solution is measured is known as [29]_____. The reaction is finished at the [30]_____, which is shown by a change in color of an [31]_____. Effects including lowering of freezing point, elevation of boiling point, and osmosis, which depend upon the concentration of solute, rather than its particular identity are called [32]_____. Solutes [33]_____ the freezing temperature of water. A solution of antifreeze in water freezes at a [34]_____ temperature and boils at a [35]_____ temperature than pure water. Solution equilibrium deals with the extent to which [36]_____ reactions proceed in a forward or backward direction. Four major classes of these reactions are [37]_____ _____. An expression such as:

$$\frac{[C]^c[D]^d}{[A]^a[B]^b} = K$$

that describes an equilibrium reaction represented by

$$aA + bB \leftrightarrows cC + dD$$

is called [38]_____. A statement of the law governing gas solubilities is [39] _____. _____ _____, which is called [40]_____. For a gas, "X," a mathematical expression of this law is [41]_____. Extremely small particles suspended uniformly in water form a [42]_____. suspension. Colloidal particles are stabilized in water by electrical [43]_____ or attraction to [44]_____. Two foods that are colloidal suspensions are [45]_____. Coagulation is a term given to the process by which colloidal particles [46] _____ _____. Water and solutes pass through certain membranes by a process called [47]_____. Because of this phenomenon, red blood cells placed in pure water [48]_____, and those placed in a solution containing much more salt than blood plasma contains will [49]_____.

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Answers to Chapter Summary

1. dissolve
2. solution
3. solute
4. solvent
5. insoluble
6. benzene, perchloroethylene, and acetone
7. hydrogen bonding and the fact that water molecules are dipoles
8. O_2 molecules
9. Na^+ and Cl^- ions
10. H^+ and Cl^- ions
11. hydronium ion, H_3O^+
12. concentration
13. million
14. ppm
15. parts per billion
16. ppb
17. moles
18. liter of solution
19. 17
20. 17 g
21. 0.25
22. $M_1 \times V_1 = M_2 \times V_2$
23. 3.75
24. $pH = -\log[H^+]$
25. acidic
26. solubility
27. saturated
28. standard solution
29. titration
30. end point
31. indicator
32. colligative properties
33. lower
34. lower
35. higher
36. reversible
37. acid-base, solubilization (precipitation), complexation, oxidation-reduction
38. an equilibrium constant expression
39. at constant temperature the solubility of a gas in a liquid is proportional to the partial pressure of the gas in contact with the liquid
40. Henry's Law
41. $[X(aq)] = K P_X$
42. colloidal
43. charge
44. water

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45. milk and mayonnaise
46. aggregate or come together
47. osmosis
48. swell
49. shrink

QUESTIONS AND PROBLEMS

Section 7.1. What are Solutions? Why are They Important?

1. Of the following, the **untrue** statement is: (a) Sugar dissolves in water. (b) When this happens, the sugar becomes the solute. (c) A solution is formed. (d) In the solution, the sugar is present as aggregates of molecules in the form of very small microcrystals. (e) The water is the solvent.
2. Is tap water a solution? If so, what does it contain besides water?
3. What does a reaction such as,

 $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

 illustrate about the role of solutions in chemical reactions?
4. Summarize the industrial uses of solutions.
5. What is the significance of solutions in the environment?

Section 7.2. Solvents

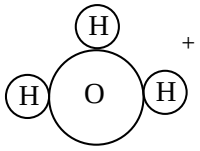
6. Why are volatile solvents especially useful in industrial applications?
7. What are some of the health considerations involved with the use of industrial solvents?

Section 7.3. Water—A Unique Solvent

8. Sketch the structure of the water molecule and explain why it is particularly significant in respect to water's solvent properties. Why is the water molecule called a dipole?
9. What are hydrogen bonds? Why are they significant in regard to water's solvent properties?

Section 7.4. The Solution Process and Solubility

10. What is represented by the following species:



What is its formula, and what are the formulas of related species? How is it formed? What is it called?

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11. Distinguish among the nature of the solution process and the species in solution for the dissolution of (a) O_2, (b) NaCl, and (c) HCl in water.

12. Why is a solution formed by dissolving HCl(*g*) in water not called a "hydrogen chloride" solution?

Section 7.5. Solution Concentrations

13. The molecular mass of ammonia, NH_3, is 17. How many grams of ammonia are in 1 liter of 2 M solution?

14. How many grams of ammonia are in 3 liters of 1 M solution?

15. How many grams of ammonia are in 3 liters of 2 M solution?

16. If one wished to prepare 2 liters of 1.2 M NaCl, how many liters of 2*M* NaCl would be required?

17. How much of a standard solution of a sodium compound containing 1000 mg of Na^+ per liter should be taken to prepare 5 liters of a standard sodium solution containing 10 mg of sodium per liter?

18. Exactly 1.50 liters of 2.00 M HCl was added to a 2.00-liter volumetric flask, and the volume brought to 2.00 liters with water. What was the molar concentration of HCl in the resulting solution?

19. Give an equation that relates molar concentration, volume of solution, mass of solute and molar mass of solute.

20. What is the process called when a measured volume of a solution is diluted with water to a specific volume? What remains the same during this process?

21. What are the relationships among the terms *neutral*, *acidic*, *basic*, and *pH*?

22. What does a *saturated* solution have to do with the *solubility* of a solute? What is meant by *supersaturated*?

23. What are the common effects of different temperatures upon the solubilities of (a) solids and (b) gases?

$$NaOH + CO_2 \text{ (not very soluble)} \rightarrow NaHCO_3 \text{ (highly soluble)}$$

Section 7.6. Standard Solutions and Titrations

24. Explain how a *standard solution*, *buret*, and *indicator* are used in *titrations*.

25. Exactly 1.00 liter of 1.00*M* HCl was added to a 2.00-liter volumetric flask. Next, a total of 0.25 mole of solid NaOH was added. After the chemical reaction between the HCl and the NaOH was complete, water was added to bring the total volume to 2.00 liters. What chemical reaction occurred when the HCl was added? How many moles of HCl were left after this reaction occurred? What was the molar concentration of HCl after the solution was diluted to 2.00 liters?

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26. A total of 2.50 liters of 0.100 M NaCl was mixed with 3.00 liters 0.0800 M NaCl. Assume that the volumes of the solutions add together to give 5.50 liters (volumes *may* not be additive with more concentrated solutions). What was the molar concentration of NaCl in the final solution?

27. What is the purpose of an equation, such as

 $M_{HCl} \times \text{Volume HCl} = M_{NaOH} \times \text{Volume NaOH}$

 in titration calculations?

Section 7.7. Physical Properties of Solutions

28. How are *colligative properties* defined and what are three major colligative properties?

29. Why is it desirable to have ethylene glycol mixed with water in an automobile's cooling system even during the summer?

30. Placed in a solution that is about 0.10 molar in sodium chloride, blood cells would be somewhat turgid, or "swollen." What property of solutions does this observation illustrate? Explain.

31. What is an *isotonic solution* ?

32. What are the nature and uses of *reverse osmosis*?

Section 7.8. Solution Equilibria

33. Consider the following generalized reaction, where all species are in solution:

 $$aA + bB \rightleftarrows cC + dD$$

 What is the significance of the **double** arrows? Explain *solution equilibrium* in the context of this reaction. Be sure to include a discussion of the *equilibrium constant expression*.

34. Match each reaction on the left with the type of equilibrium that it represents on the right, below:

1. $Fe^{3+} + SCN^- \rightleftarrows FeSCN^{2+}$	(a) Oxidation-reduction
2. $AgCl(s) \rightarrow Ag^+ + Cl^-$	(b) Solubility
3. $HAc \rightleftarrows H^+ + Ac^-$	(c) Acid–base
4. $MnO_4^- + 5Fe^{2+} + 8H^+ \rightleftarrows Mn^{2+} + 5Fe^{3+} + 4H_2O$	(d) Complex ion formation

35. Name, state, and give the mathematical expression for the law that describes the following kind of equilibrium:

 $X(g) \rightleftarrows X(aq)$

36. How do reactions such as the ones below affect gas solubility?

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$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$

$SO_2 + HCO_3^-$ (From water alkalinity) $\leftrightarrows CO_2 + HSO_3^-$

37. What does the equation,

$$P_{O_2} = (1.0000 \text{ atm} - 0.0313 \text{ atm}) \times 0.2095 = 0.2029 \text{ atm}$$

express? What is the "0.0313 atm?"

Section 7.9. Colloidal Suspensions

38. Describe the nature and characteristics of *colloidal particles* that are in colloidal suspension in water. What is there about colloidal particles that causes them to exhibit the *Tyndall effect*?

39. Distinguish among *hydrophilic colloids*, *hydrophobic colloids*, and *association colloids*. Which consist of *micelles*? What are micelles?

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Manahan, Stanley E. "CHEMISTRY AND ELECTRICITY"
Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

8 CHEMISTRY AND ELECTRICITY

8.1 CHEMISTRY AND ELECTRICITY

Electricity can have a strong effect on chemical systems. For example, passing electricity through a solution of sodium sulfate in water breaks the water down into H_2 gas and O_2 gas. In Section 6.3 it was discussed how solutions of completely ionized strong electrolytes conduct electricity well, weak electrolytes conduct it poorly, and nonelectrolytes not at all. Electrical current basically involves the activity of electrons, as well as their flow and exchange between chemical species. Since electrons are so important in determining the chemical bonding and behavior of atoms, it is not surprising that electricity is strongly involved with many chemical processes.

The exchange of electrons between chemical species is part of the more general phenomenon of oxidation-reduction, which is defined in more detail in Section 8.2. Oxidation-reduction processes are of particular importance in environmental chemistry. Organic pollutants are degraded and nutrient organic matter utilized for energy and as a carbon source for biomass by oxidation-reduction reactions involving fungi in water and soil. The nature of inorganic species in water and soil depends upon whether the medium is oxidizing (oxygen present, low electron activity) or reducing (O_2 absent, high electron activity). Strong oxidants, such as ozone (O_3), and organic peroxides formed by photochemical processes in polluted atmospheres, are noxious pollutants present in photochemical smog.

The flow of electricity through a chemical system can cause chemical reactions to occur. Similarly, chemical reactions may be used to produce electricity. Such phenomena are called **electrochemical phenomena** and are covered under the category of **electrochemistry**. Examples of electrochemistry abound. The transmission of nerve impulses in animals, and even human thought processes, are essentially electrochemical. A dry cell produces electricity from chemical reactions. An automobile storage battery stores electrical energy as chemical energy, and reverses the process when it is discharged. An electrochemical process called

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electrodialysis can be used for the purification of water. The analytical chemist can use an electrical potential developed at a probe called a glass electrode to measure the pH of water. Obviously, the electrical aspects of chemistry are important; they are covered in this chapter.

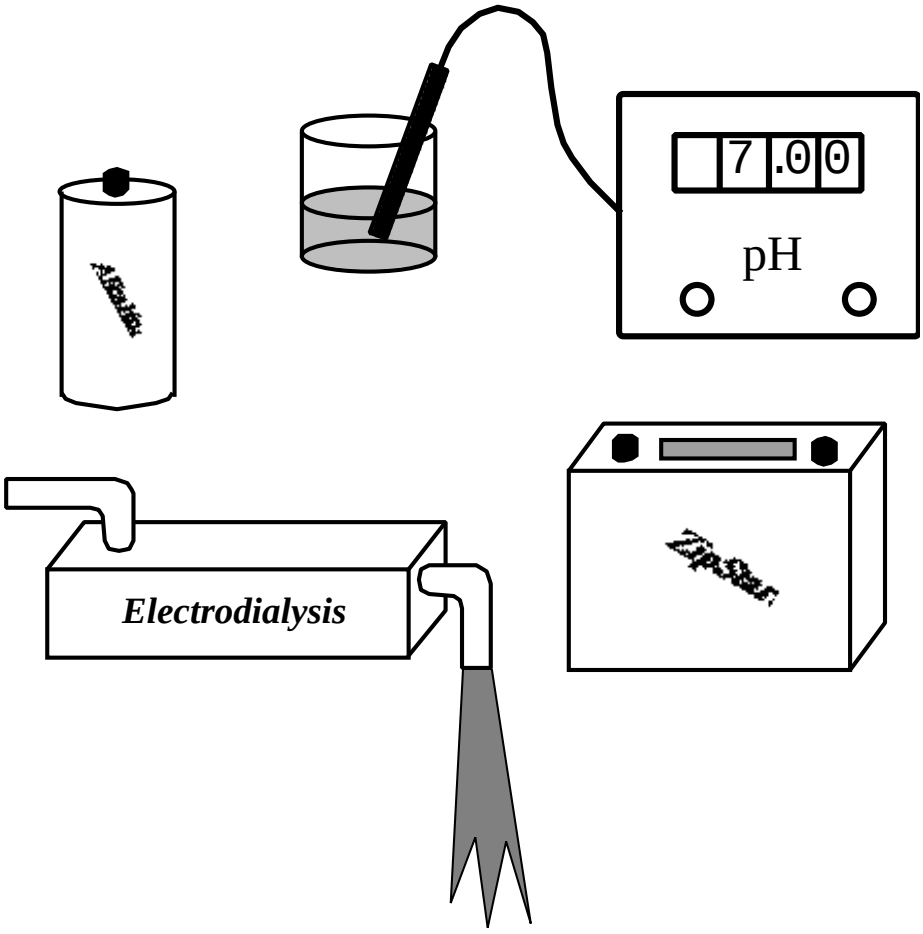


Figure 8.1 The interaction of electricity and chemistry is an important phenomenon in many areas.

8.2 OXIDATION AND REDUCTION

It has been seen that many chemical reactions can be regarded as the transfer of electrically charged electrons from one atom to another. Such a transfer can be arranged to occur through a wire connected to an electrode in contact with atoms that either gain or lose electrons. In that way, electricity can be used to bring about chemical reactions, or chemical reactions can be used to generate electricity. First, however, consider the transfer of electrons between atoms that are in contact with each other.

An oxygen atom, which has a strong appetite for electrons, accepts 2 valence (outer shell) electrons from a calcium atom,

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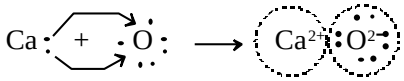
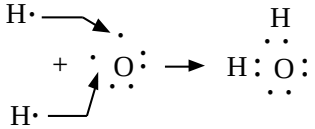


Figure 8.2 Oxygen atoms have a strong tendency to accept electrons, and an atom that has lost electrons is said to be oxidized.

to form a calcium ion, Ca^{2+}, and an oxide ion, O^{2-}. The loss of electrons by the calcium atom is called **oxidation**, and it is said to have been **oxidized**. These terms are derived from the name of oxygen because of its tendency to take electrons from other atoms, such as calcium. The gain of electrons by the oxygen is called **reduction**, and the oxygen atom has been **reduced**; atoms that gain electrons in a transfer such as this are always reduced. The overall reaction is called an **oxidation-reduction reaction**, sometimes abbreviated as **redox**. Oxidation and reduction always occur together. Whenever something is oxidized, something else is always reduced. In this case, Ca is oxidized when O is reduced.

It is easy to see what is meant by oxidation and reduction when there is a transfer of electrons to form ionic bonds (see Section 4.3). However, the concept can be extended to compounds that are bonded together by covalent bonds. For example, when H combines with O to form H_2O,



(8.2.1)

electrons are shared between H and O atoms in the covalent bonds joining them together. However, the sharing is not equal because the O atom has a much stronger tendency to grab onto electrons. Therefore, the O atom is regarded as "taking" an electron from each of the H atoms. If O really did take both of these electrons completely away from H, it would have a -2 charge. Although the oxygen does not have a charge as such, the oxygen atom in H_2O is assigned an oxidation number with a value of -2 because of its tendency to attract the 2 electrons from the 2 H atoms. The oxidation number is the hypothetical charge that an atom would have if it gained or lost a particular number of electrons when it formed a chemical coumpound. In virtually all cases encountered in this book, the oxidation number of chemically combined O is -2. In H_2O, each H atom can be visualized as losing its electron to the O atom because of the unequal sharing. This gives H an oxidation number of +1. In practically all the compounds encountered in this book, the oxidation number of chemically combined H is +1.

The oxidation number of any element is zero in the elemental form. Therefore, the oxidation number of O in O_2 is zero, and the oxidation number of H in H_2 is zero.

Figure 8.3 gives the oxidation numbers of the chemically combined forms of the first 20 elements in the periodic table. From this table, observe that the chemically combined forms of the elements in the far left column (H plus the alkali metals, Li, Na, and K) have an oxidation number of +1. Those in the next column over (the alkaline earths, Be, Mg, and Ca) have an oxidation number of +2 and those in the

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following column (B and Al) have an oxidation number of +3. It has already been mentioned that O almost always has an oxidation number of -2. That of F is always -1. The oxidation number of chemically combined Cl is generally -1. As shown in Figure 8.3, the oxidation numbers of the other elements are variable.

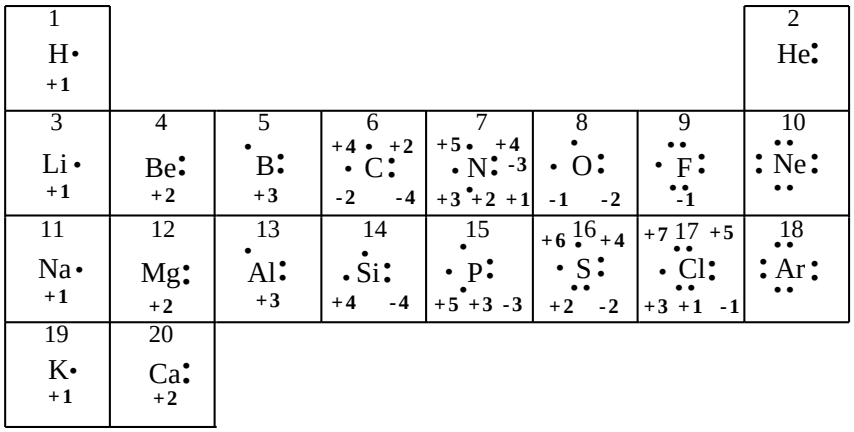


Figure 8.3 Common oxidation numbers of the chemically combined forms of the first 20 elements (small bold-faced numbers).

Table 8.1 Oxidation Numbers of Elements in Some Compounds and Ions

Compound or ion	Element whose oxidation number is to be calculated	Oxidation number of element
SO_2	S	+4
SO_3	S	+6
NH_3	N	-3
CH_4	C	-4
HNO_3	N	+5
Na_3PO_4	P	+5
CO_3^{2-}	C	+4
NO_2^-	N	+3

Even though the oxidation numbers of some elements vary, they can usually be figured out by applying the following rules:

- The sum of the oxidation numbers of the elements in a compound equals 0.
- The sum of the oxidation numbers of the elements in an ion equals the charge on the ion.

The application of these rules can be seen in Table 8.1. For each compound in this table, the oxidation number of each element, except for one, is definitely known. For

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example, in SO_2, each O has an oxidation number of -2. There are 2 Os for a total of -4. The -4 must be balanced with a +4 for S. In SO_3, the total of -6 for 6 Os, each with an oxidation number of -2, must be balanced with a +6 for S. In Na_3PO_4, each Na has an oxidation number of +1, and each O has -2. Therefore, the oxidation number of P is calculated as follows:

3 Na times +1 per Na = +3
4 O times -2 per O = -8

That leaves a sum of -5, which must be balanced with a +5

(+3 for 3 Na) + (x for 1 P) + (-8 for 4 O) = 0

x = oxidation number of P = 0 -3 + 8 = 5 (8.2.2)

In the NO_2^- ion, each of the 2 Os has an oxidation number of -2, for a total of -4. The whole ion has a net charge of -1, so that the oxidation number of N is only +3.

8.3 OXIDATION-REDUCTION IN SOLUTION

Many important oxidation-reduction reactions occur involving species dissolved in solution. Many years ago, a struggling college student worked during the summer in a petroleum refinery to earn money for the coming academic year. One of the duties assigned to the labor gang at that time involved carrying a solution of copper sulfate, $CuSO_4$, dissolved in water, from one place to another. Castoff steel buckets were used for that purpose. After about the fifth or sixth trip, the bottom would drop out of the bucket, spilling the copper sulfate solution on the ground. This unfortunate phenomenon can be explained by an oxidation-reduction reaction. $CuSO_4$ dis-

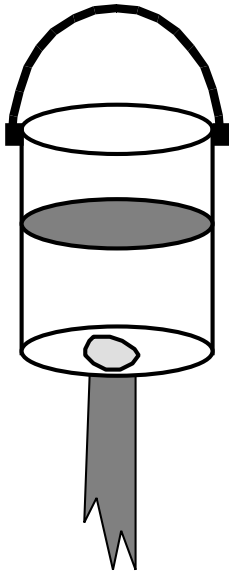


Figure 8.4 A solution of $CuSO_4$ in a steel bucket soon eats its way through the steel, allowing a leak to occur.

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solved in water, is present as Cu^{2+} and SO_4^{2-} ions. The Cu^{2+} ion acts as an oxidizing agent and reacts with the iron (Fe) in the bucket as follows:

$$\underset{\text{copper(II) sulfate}}{Cu^{2+} + SO_4^{2-}} + Fe \rightarrow \underset{\text{iron(II) sulfate}}{Fe^{2+} + SO_4^{2-}} + Cu \qquad (8.3.1)$$

This results in the formation of a solution of iron(II) sulfate and leaves little pieces of copper metal in the bottom of the bucket. A hole is eventually eaten through the side or bottom of the bucket as the iron goes into solution.

The kind of reaction just described is used in a process called **cementation** to purify some industrial wastewaters that contain dissolved metal ions. The water is allowed to flow over iron scraps, and so-called heavy metal ions, such as Cu^{2+}, Cd^{2+}, and Pb^{2+} precipitate from solution as they are replaced by Fe^{2+}. Cementation results in the replacement of poisonous heavy metal ions in solution by relatively harmless iron.

The reaction of iron and copper sulfate involves the transfer of electrons. These electrons can be forced to go through a wire as electricity and do useful work. To do that, an **electrochemical cell** would be set up as shown in Figure 8.5.

As may be seen, Cu and a $CuSO_4$ solution are kept in a container that is separated from a bar of Fe dipping into a solution of $FeSO_4$. These two containers are called **half-cells**. On the left side, Cu^{2+} is reduced to Cu by the **reduction half-reaction**,

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad (8.3.2)$$

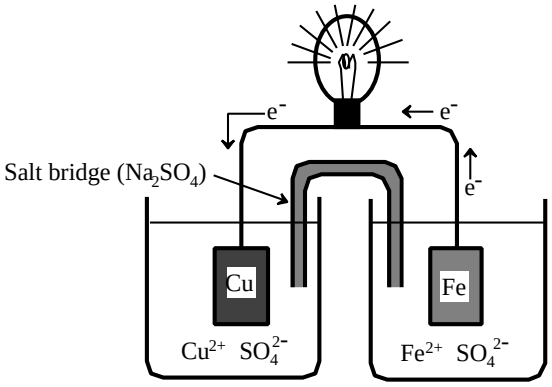


Figure 8.5 An electrochemical cell

The electrons required for the reduction of Cu^{2+} are picked up from the bar of copper. On the right side, Fe is oxidized by the **oxidation half-reaction**,

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (8.3.3)$$

In this case the electrons are left behind on the iron bar, and they go through a wire to the copper bar. In so doing, they may be forced through a light bulb or electric motor and made to do useful work. This is an example of the conversion of chemical energy to electrical energy. The salt bridge shown in Figure 8.5 is just a tube filled

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with a solution of a salt, such as Na_2SO_4. It completes the circuit by allowing charged ions to move between the two half-cells so that neither has an excess of positive or negative charge. The two half-reactions can be added together,

$$\begin{array}{rcl} Cu^{2+} + 2e & \rightarrow & Cu \\ Fe & \rightarrow & Fe^{2+} + 2e \\ \hline Cu^{2+} + Fe & \rightarrow & Fe^{2+} + Cu \end{array} \qquad (8.3.4)$$

to give the total reaction that occurs in the electrochemical cell. Recall that it is the same reaction that occurs when $CuSO_4$ solution contacts iron in a steel bucket (when that reaction was written, SO_4^{2-} was shown as a spectator ion—one that does not take part in the reaction).

For an electrical current to flow and light up the bulb shown in Figure 8.5, there must be a **voltage difference** (difference in electrical potential) between the iron and copper bar. These bars are used to transfer electrons between a wire and solution, and in this case, they actually participate in the oxidation-reduction reaction that occurs. The metal bars are called **electrodes**. Because this cell is used to generate a voltage and to extract electricity from a chemical reaction, it is called a **voltaic cell**.

8.4 THE DRY CELL

Dry cells are used as sources of portable electrical energy for flashlights, radios, portable instruments, and many other devices. As shown in Figure 8.6, a dry cell consists of a graphite (carbon) rod in the center of a zinc cylinder, which is filled with a moist paste of manganese dioxide, ammonium chloride, and carbon black. The

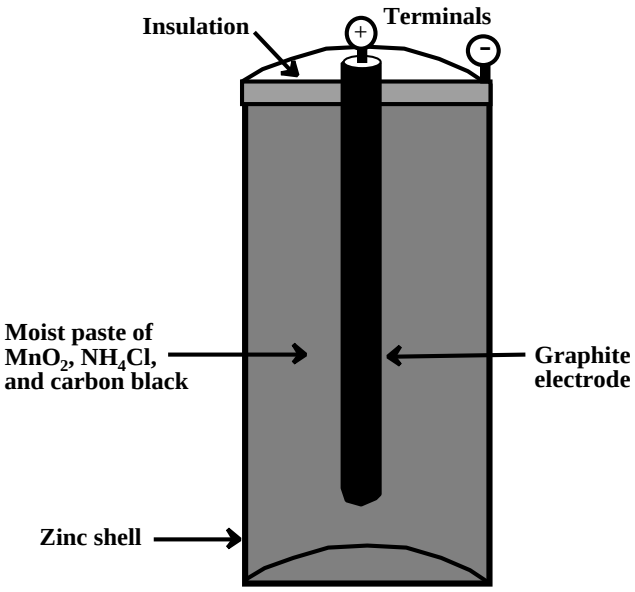


Figure 8.6 The dry cell.

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carbon rod and the zinc cylinder make up the two electrodes in the dry cell. When the two terminals on the electrodes are connected, such as through an electrical circuit powering a portable radio, half-reactions occur at both electrodes. At the graphite electrode the half-reaction is,

$$MnO_2(s) + NH_4^+(aq) + e^- \rightarrow MnO(OH)(s) + NH_3(aq) \quad (8.4.1)$$

where abbreviations have been used to show which of the materials are solids (*s*) and which are dissolved in water (*aq*). This half-reaction takes negatively charged electrons away from the graphite electrode, leaving it with a + charge. It is a reduction half-reaction. The electrode at which reduction occurs is always called the **cathode**. Therefore, the graphite rod is the cathode in a dry cell. The half-reaction that occurs at the zinc electrode is,

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^- \quad (8.4.2)$$

This reaction leaves a surplus of negatively charged electrons on the zinc electrode, so that it has a - charge. It is an oxidation reaction. The electrode at which oxidation occurs in an electrochemical cell is always called the **anode**. If the two electrodes are connected, electrons will flow from the zinc anode to the carbon cathode. Such a flow of electrons is an electrical current from which useful work can be extracted. Every time 2 MnO_2 molecules are reduced, as shown in the first half-reaction, one Zn is oxidized. Therefore, the overall oxidation-reduction reaction is obtained by multiplying everything in the reduction half-reaction at the cathode by 2 and adding it to the oxidation half-reaction that occurs at the anode. The 2 e^- cancel on both sides of the equation yielding the following overall oxidation-reduction reaction:

$$2MnO_2(s) + 2NH_4^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2MnO(OH)(s) + 2NH_3(aq) \quad (8.4.3)$$

8.5 STORAGE BATTERIES

One of society's generally faithful technological servants is the lead storage battery used in automobiles. This kind of battery provides a steady source of electricity for starting, lights, and other electrical devices on the automobile. Unlike the electrochemical cells already discussed, it can both store electrical energy as chemical energy and convert chemical energy to electrical energy. In the former case, it is being charged, and in the latter case it is being discharged.

A 12-volt lead storage battery actually consists of 6 electrochemical cells, each delivering 2 volts. The simplest unit of a lead storage battery that can be visualized consists, in the charged state, of two lead grids, one of which is covered by a layer of lead dioxide, PbO_2. These two electrodes are immersed in a sulfuric acid solution, as shown in Figure 8.7. When the battery is discharged, the pure lead electrode acts as an anode where the oxidation reaction occurs. This reaction is,

$$Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^- \quad (8.5.1)$$

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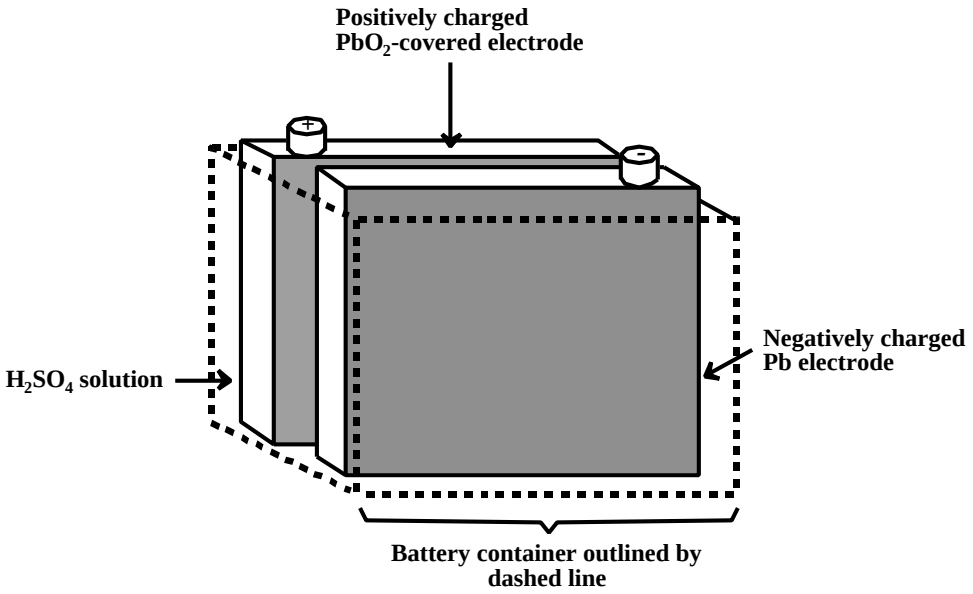


Figure 8.7 Two electrodes from a lead storage battery.

in which a layer of solid lead sulfate, $PbSO_4$, is plated onto the lead electrode. The PbO_2 on the other electrode is reduced as part of the cathode reaction:

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O \qquad (8.5.2)$$

The electrons needed by this half-reaction are those produced at the anode. These electrons are forced to go through the battery leads and through the automobile's electrical system to do useful work. Adding these two half-reactions together gives the overall reaction that occurs as the battery is discharged:

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O \qquad (8.5.3)$$

As the battery is discharged, solid $PbSO_4$ is deposited on both electrodes.

As the battery is charged, everything is reversed. The half-reactions and overall reaction are,

$$\begin{aligned} &\text{Cathode: } PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-} \\ &\underline{\text{Anode: } PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-} \\ &\text{Overall: } 2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \end{aligned} \qquad (8.5.4)$$

Another kind of battery that is frequently used is the rechargeable nickel-cadmium battery employed in electronic calculators, electronic camera flash attachments, and other applications. During discharge, the reactions that occur in this battery are,

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Cathode: $NiO_2 + 2H_2O + 2e^- \rightarrow Ni(OH)_2 + 2OH^-$

Anode: $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$

Overall: $Cd + NiO_2 + 2H_2O \rightarrow Cd(OH)_2 + Ni(OH)_2$ (8.5.5)

As the battery is being charged, both half-reactions and the overall reaction are simply reversed. Larger versions of the "Nicad" battery are used in some automobiles and motorcycles.

High-capacity, readily charged storage batteries are very important to the success of newly developing electrically powered vehicles. The successful development and widespread use of such vehicles would be very helpful in alleviating atmospheric pollution problems, such as carbon monoxide emissions and photochemical smog.

8.6 USING ELECTRICITY TO MAKE CHEMICAL REACTIONS OCCUR

Electricity is commonly used as an energy source to make chemical reactions occur that do not occur by themselves. Such a reaction is called an **electrolytic reaction**. The cell in which it occurs is an **electrolytic cell** (Figure 8.8). A direct electrical current passing through a solution of a salt in water causes the water to break up and form H_2 and O_2. The process can now be examined in a little more detail. As always, oxidation occurs at the anode. In this case, the external electrical

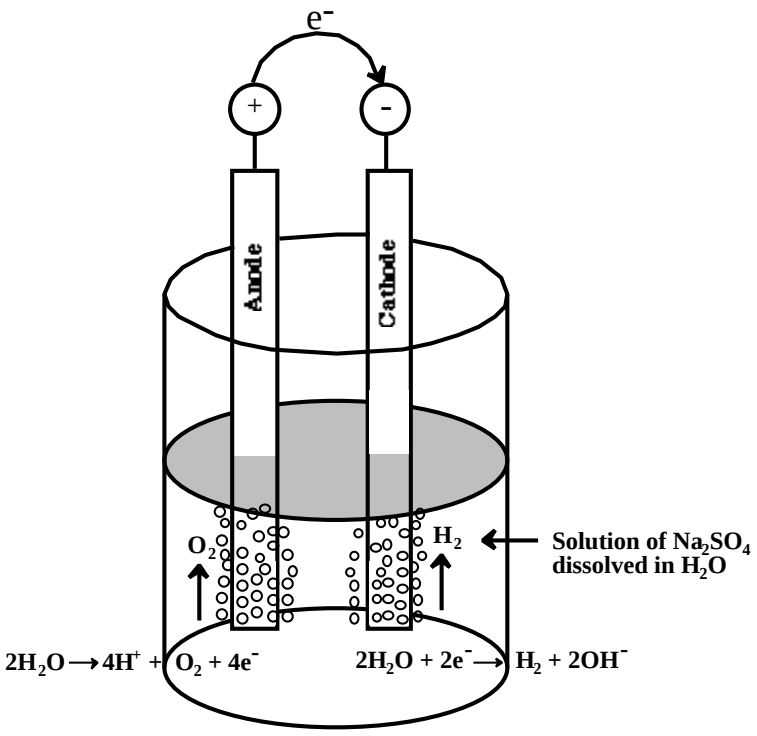


Figure 8.8 The electrolysis of water to form H_2 and O_2.

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power supply withdraws electrons from the anode, which in turn takes electrons away from water, as shown for the following oxidation half-reaction:

$$2H_2O \rightarrow 4H^+ + O_2(g) + 4e^- \quad (8.6.1)$$

As a result, oxygen gas, O_2, is given off at the anode. The power supply forces electrons onto the cathode, where the following reduction half-reaction occurs

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \quad (8.6.2)$$

As a result, hydrogen gas is produced at the cathode. The H^+ ions produced at the anode and the OH^- ions produced at the cathode combine according to the neutralization reaction,

$$H^+ + OH^- \rightarrow H_2O \quad (8.6.3)$$

The overall electrolysis reaction is,

$$2H_2O + \text{electrical energy} \rightarrow 2H_2(g) + O_2(g) \quad (8.6.4)$$

Electrolytic processes are widely used to manufacture chemicals. One of the simplest of these is the Downs process for manufacturing liquid sodium. This chemically active metal is used to synthesize organic compounds, such as tetraethyl lead once widely used as a gasoline additive, and in many other applications. It is made by passing an electrical current through melted sodium chloride, as shown in Figure 8.9.

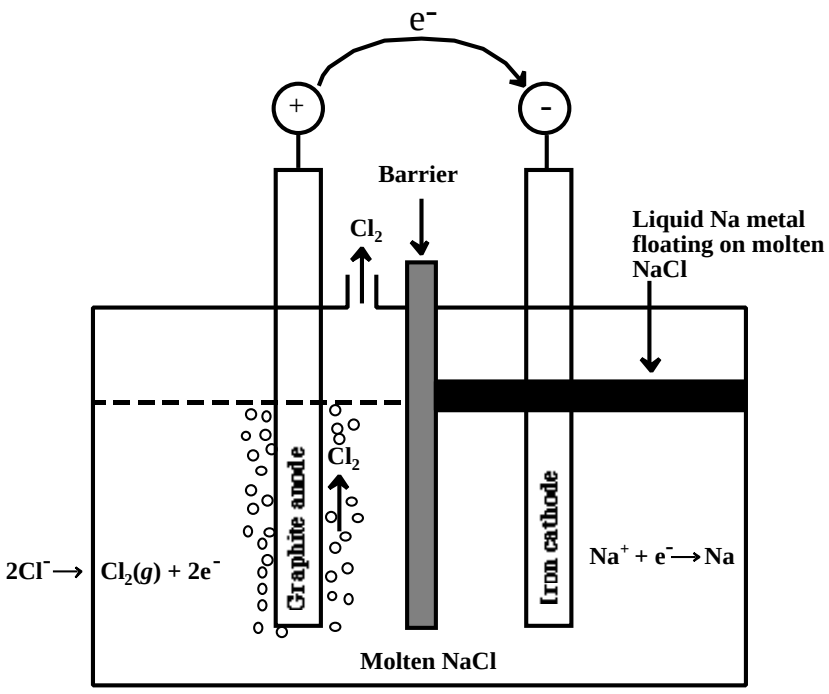


Figure 8.9 Electrolysis of melted NaCl to produce liquid sodium metal and chlorine gas.

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Electrons forced onto the iron cathode by the external source of electricity bring about the reduction half-reaction,

$$Na^+ + e^- \rightarrow Na \quad (8.6.5)$$

Withdrawal of electrons from the graphite anode by the external electrical circuit applies the driving force for the oxidation half-reaction:

$$2Cl^- \rightarrow Cl_2(g) + 2e^- \quad (8.6.6)$$

The overall oxidation-reduction reaction is,

$$2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2(g) \quad (8.6.7)$$

In industrial practice, a Downs cell is especially designed to prevent contact of the Na and Cl_2, which would, of course, react violently with each other.

The Cl_2 that is produced during the manufacture of liquid Na is a valuable byproduct that is used to manufacture chlorinated solvents, pesticides, and in other applications. Far more Cl_2 is needed than sodium. More economical processes involving the electrolysis of NaCl solutions in water are used to manufacture Cl_2 along with NaOH.

8.7 ELECTROPLATING

One of the most common uses of electrochemistry is the plating of a thin layer of an expensive or attractive metal onto a base of cheaper metal. The shiny layer of chromium metal that used to be very common on automobile bumpers and other trim before it became too expensive for this application is plated onto steel with an electrochemical process. A thin layer of silver is commonly plated onto "silverware" to make eating utensils look like the "real thing" using an electrochemical process. The use of electrochemistry for plating metals onto surfaces is called **electroplating**.

Many electroplating processes are actually quite complicated. However, an idea of how these processes work can be gained by considering the electroplating of silver metal onto a copper object, as shown in Figure 8.10. The copper object and a piece of silver metal make up the two electrodes. They are dipped into a solution containing dissolved silver nitrate, $AgNO_3$, and other additives that result in a smooth deposit of silver metal. Silver ion in solution is reduced at the negatively charged cathode,

$$Ag^+ + e^- \rightarrow Ag \quad (8.7.1)$$

leaving a thin layer of silver metal. The silver ion is replaced in solution by oxidation of silver metal at the silver metal anode:

$$Ag \rightarrow Ag^+ + e^- \quad (8.7.2)$$

Electroplating is commonly used to prevent corrosion (rusting) of metal. Zinc metal electroplated onto steel prevents rust. The corrosion of "tin cans" is inhibited by a very thin layer of tin plated onto rolled steel.

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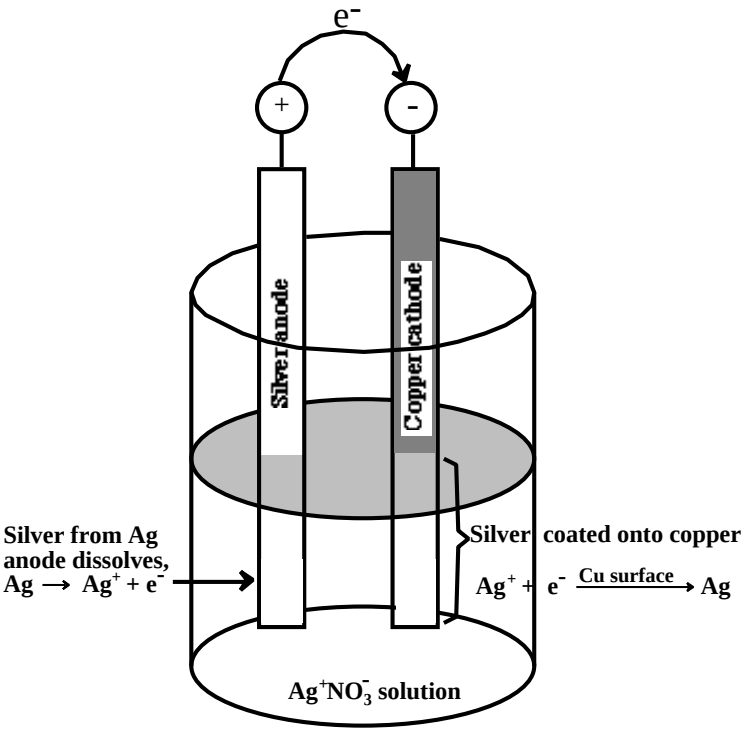


Figure 8.10 Electrochemical cell for electroplating silver onto copper.

8.8 FUEL CELLS

Current methods for the conversion of chemical energy to electrical energy are rather cumbersome and wasteful. Typically, coal is burned in a boiler to generate steam, the steam goes through a turbine, the turbine drives a generator, and the generator produces electricity. This whole process wastes about 60% of the energy originally in the coal. More energy is wasted in transmitting electricity through power lines to users. It is easy to see the desirability of converting chemical energy directly to electricity. This can be done in fuel cells.

A fuel cell that uses the chemical combination of H_2 and O_2 to produce electricity directly from a chemical reaction is shown in Figure 8.11. This device consists of two porous graphite (carbon) electrodes dipping into a solution of potassium hydroxide, KOH. At the anode, H_2 is oxidized, giving up electrons, and at the cathode, O_2 is reduced, taking up electrons. The two half-reactions and the overall chemical reaction are,

$$\text{Anode: } 2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$$

$$\text{Cathode: } O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

$$\text{Overall: } 2H_2 + O_2 \rightarrow 2H_2O \qquad (8.8.1)$$

This reaction obviously provides a non-polluting source of energy. Unfortunately,

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both hydrogen and oxygen are rather expensive to generate.

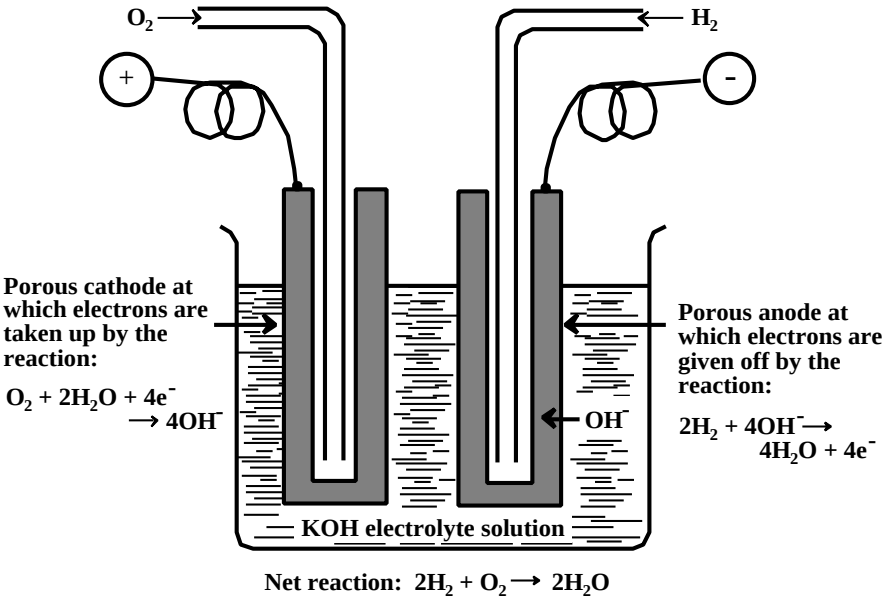
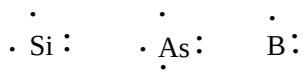


Figure 8.11 Fuel cell for direct production of electricity by oxidation of hydrogen.

8.9 SOLAR CELLS

The direct conversion of light energy to electrical energy can be accomplished in **photovoltaic cells**, also called **solar cells**. These consist basically of two layers of silicon, Si, one **doped** with about 1 atom per million of arsenic, As, and the other doped with about 1 atom per million of boron, B. To understand what happens, consider the Lewis symbols of the three elements involved:



As shown by its Lewis symbol above and discussed in Chapter 3, each silicon atom has 4 valence electrons. In a crystal of Si, each of the silicon atoms is covalently bonded to 4 other Si atoms, as shown in Figure 8.12. If a B atom replaces one of the Si atoms, the 3 valence electrons in B result in a shortage of 1 electron, leaving what is called a **positive hole**. Each As atom has 5 valence electrons, so that replacement of one of the Si atoms by As leaves a surplus of 1 electron, which can move about in the Si crystal. A layer of Si atoms doped with As makes up a **donor** layer because of the "extra" valence electron introduced by each As, atom and Si doped with B makes up an **acceptor** layer because each B atom has 1 less valence electron than does each Si atom. When two such layers are placed in contact, the positive holes near the surface of the acceptor layer become filled with excess electrons from the donor layer. Nothing else happens unless light falls on the solar cell. This light provides the energy required to push electrons back across the boundary. These electrons can be withdrawn by a wire from the donor layer and returned by a wire to the acceptor layer, resulting in a flow of usable electrical current.

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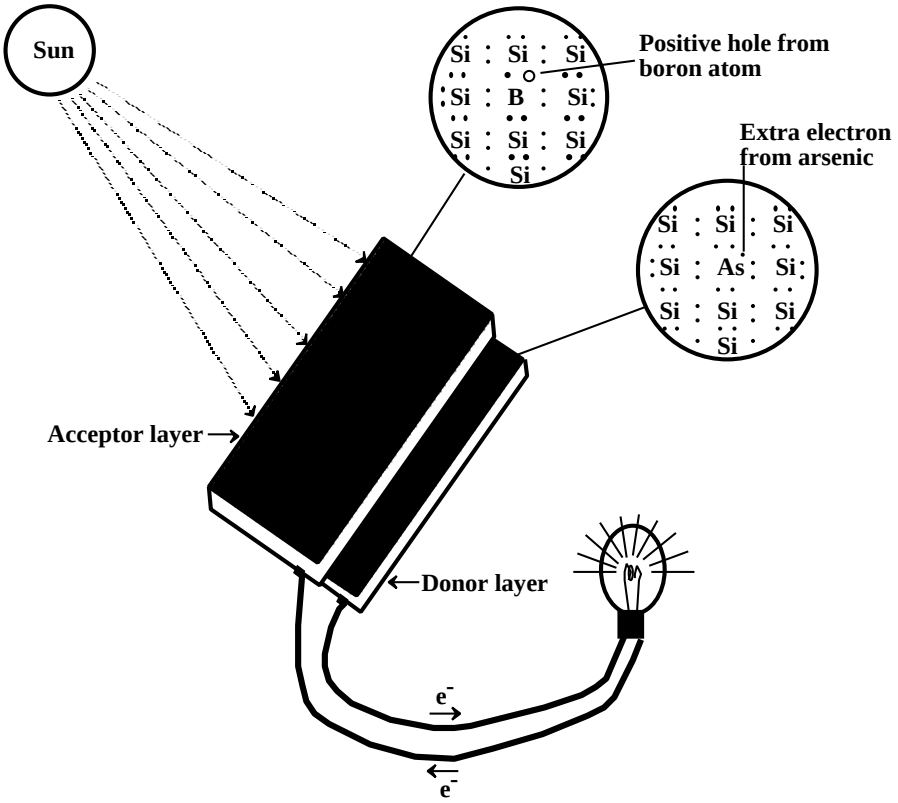


Figure 8.12 A photovoltaic cell. Note the positive hole, ○, at the site of the B atom, and the extra electron around the As atom.

8.10 REACTION TENDENCY

It has already been seen that whole oxidation-reduction reactions can be constructed from half-reactions. The direction in which a reaction goes is a function of the relative tendencies of its constituent half-reactions to go to the right or left. These tendencies, in turn, depend upon the concentrations of the half-reaction reactants and products and their relative tendencies to gain or lose electrons. The latter is expressed by a **standard electrode potential**, $\mathbf{E^0}$. The tendency of the whole reaction to proceed to the right as written is calculated from the **Nernst equation**, which contains both E^0 and the concentrations of the the reaction participants. These concepts are explained further in this section and the following section.

Measurement of E^0

To visualize the measurement of E^0, consider the electrochemical cell shown in Figure 8.13. When the two electrodes are connected by an electrical conductor, the reaction

$$2Ag^+ + H_2 \leftarrow \rightarrow 2H^+ + 2Ag \qquad (8.10.1)$$

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occurs in which hydrogen gas would reduce silver ion to silver metal. This reaction is composed of the two following half-reactions:

$$2Ag^+ + 2e^- \leftarrow\rightarrow 2Ag \qquad E^0 = 0.7994 \text{ volt} \qquad (8.10.2)$$

$$-(2H^+ + 2e^- \leftarrow\rightarrow H_2 \qquad E^0 = 0.00 \text{ volt}) \qquad (8.10.3)$$

$$2Ag^+ + H_2 \leftarrow\rightarrow 2H^+ + 2Ag \qquad E^0 = 0.7994 \text{ volt} \qquad (8.10.1)$$

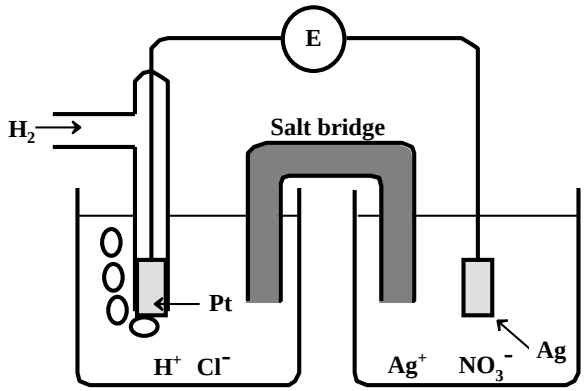


Figure 8.13 Electrochemical cell in which the reaction $2Ag^+ + H_2 \leftarrow\rightarrow 2Ag + 2H^+$ can be carried out in two half-cells.

If, in the cell shown in Figure 8.13, the activities of both Ag^+ and H^+ were exactly 1 (approximated by concentrations of 1 mol/L) and the pressure of H_2 exactly 1 atm, the potential registered between the two electrodes by a voltmeter, "E," would be 0.7994 volt. The platinum electrode, which serves as a conducting surface to exchange electrons, would be negative because of the prevalent tendency for H_2 molecules to leave negatively-charged electrons behind on it as they go into solution as H^+ ions. The silver electrode would be positive because of the prevalent tendency for Ag^+ ions to pick up electrons from it and to be deposited as Ag atoms.

The left electrode shown in Figure 8.13 is of particular importance because it is the standard electrode against which all other electrode potentials are compared. It is called the **standard hydrogen electrode**, **SHE** and has been assigned a value of exactly 0 volts by convention; its half-reaction is written as the following:

$$2H^+ + 2e^- \leftarrow\rightarrow H_2 \qquad E^0 = +0.00 \text{ volts} \qquad (8.10.3)$$

The measured potential of the right-hand electrode in Figure 8.13 versus the standard hydrogen electrode is called the **electrode potential, E.** If Ag^+ and other ions in solution are at unit activity (approximated by a concentration of 1 mole/liter), the potential is the **standard electrode potential**, $\mathbf{E^0}$. The standard electrode potential for the Ag^+/Ag couple is 0.7994 volt, expressed conventionally as follows:

$$Ag^+ + e^- \leftarrow\rightarrow Ag \qquad E^0 = 0.7994 \text{ volt} \qquad (8.10.2)$$

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E^0 Values and Reaction Tendency

Recall that half-reactions can be combined to give whole reactions and that half-reactions can occur in separate half-cells of an electrochemical cell. The inherent tendency of a half-reaction to occur is expressed by a characteristic E^0 value. In favorable cases, E^0s of half-reactions can be measured directly versus a standard hydrogen electrode by a cell such as the one shown in Figure 8.13, or they can be calculated from thermodynamic data. Several half-reactions and their E^0 values are given below:

$Cl_2 + 2e^- \leftarrow\rightarrow 2Cl^-$	$E^0 = 1.359$ volt	(8.10.4)
$O_2 + 4H^+ + 4e^- \leftarrow\rightarrow 2H_2O$	$E^0 = 1.229$ volt	(8.10.5)
$Ag^+ + e^- \leftarrow\rightarrow Ag$	$E^0 = 0.7994$ volt	(8.10.2)
$Fe^{3+} + e^- \leftarrow\rightarrow Fe^{2+}$	$E^0 = 0.771$ volt	(8.10.6)
$Cu^{2+} + 2e^- \leftarrow\rightarrow Cu$	$E^0 = 0.337$ volt	(8.10.7)
$2H^+ + 2e^- \leftarrow\rightarrow H_2$	$E^0 = 0.00$ volt	(8.10.3)
$Pb^{2+} + 2e^- \leftarrow\rightarrow Pb$	$E^0 = -0.126$ volt	(8.10.8)
$Zn^{2+} + 2e^- \leftarrow\rightarrow Zn$	$E^0 = -0.763$ volt	(8.10.9)

Basically, the E^0 values of these half-reactions express the tendency for the reduction half-reaction to occur when all reactants and products are present at unit activity; the more positive the value of E^0, the greater the tendency of the reduction half-reaction to proceed. (In a simplified sense, the activity of a substance is 1 when its concentration in aqueous solution is 1 mole/liter, its pressure as a gas is 1 atm, or it is present as a solid.) With these points in mind, examination of the E^0 values above show the following:

- The highest value of E^0 shown above is for the reduction of Cl_2 gas to Cl^- ion. This is consistent with the strong oxidizing tendency of Cl_2; chlorine much "prefers" to exist as chloride ion rather than highly reactive Cl_2 gas.
- The comparatively high E^0 value of 0.7994 volt for the reduction of Ag^+ ion to Ag metal indicates that silver is relatively stable as a metal, which is consistent with its uses in jewelry and other applications where resistance to oxidation is important.
- The value of exactly $E^0 = 0.000$ volt is assigned by convention for the half-reaction in which H^+ ion is reduced to H_2 gas; all other E^0s are relative to this value.
- The lowest (most negative) E^0 value shown above is -0.763 volt for the half-reaction $Zn^{2+} + 2e^- \leftarrow\rightarrow Zn$. This reflects the strong tendency for

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zinc to leave the metallic state and become zinc ion; that is, the half reaction tends to lie strongly to the left. Since zinc metal gives up electrons when it is oxidized to Zn^{2+} ion, zinc metal is a good reducing agent.

Half-reactions and their E^0 values can be used to explain observations such as the following: A solution of Cu^{2+} flows through a lead pipe and the lead acquires a layer of copper metal through the reaction

$$Cu^{2+} + Pb \rightarrow Cu + Pb^{2+} \qquad (8.10.10)$$

This reaction occurs because the copper(II) ion has a greater tendency to acquire electrons than the lead ion has to retain them. This reaction can be obtained by subtracting the lead half-reaction, Equation 8.10.8, from the copper half-reaction, Equation 8.10.7:

$$\begin{array}{ll} Cu^{2+} + 2e^- \leftarrow\rightarrow Cu & E^0 = 0.337 \text{ volt} \\ -(Pb^{2+} + 2e^- \leftarrow\rightarrow Pb & E^0 = -0.126 \text{ volt}) \\ \hline Cu^{2+} + Pb \leftarrow\rightarrow Cu + Pb^{2+} & E^0 = 0.463 \text{ volt} \end{array} \qquad (8.10.10)$$

The appropriate mathematical manipulation of the E^0s of the half-reactions enables calculation of an E^0 for the overall reaction, the positive value of which indicates that Reaction 8.10.10 tends to go to the right as written. This is in fact what occurs when lead metal directly contacts a solution of copper(II) ion. Therefore, if a waste solution containing copper(II) ion, a relatively innocuous pollutant, comes into contact with lead in plumbing, toxic lead may go into solution.

Based on the above calculation, if the electrochemical cell shown in Figure 8.14 were set up with activities of both Cu^{2+} and Pb^{2+} at exactly 1 (approximated by concentrations of 1 mole/liter), the potential registered by "E," a meter that measures voltage, but does not allow any current to flow, would be 0.463 volts. The lead electrode would be negative because the reaction tendency is for Pb metal to give up negative electrons to the external circuit and go into solution as Pb^{2+} ion, whereas Cu^{2+} ions tend to remove electrons from the copper electrode, giving it a + charge and coming out of solution as Cu metal. The effects of different concentrations on the potential that would be measured in such a cell are discussed in the following section.

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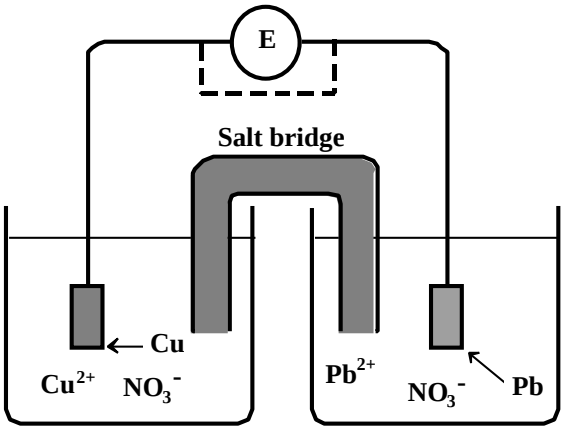


Figure 8.14 Electrochemical cell in which the tendency for the reaction $Cu^{2+} + Pb \rightleftarrows Cu + Pb^{2+}$ can be measured. In this configuration, "E" has a very high resistance and current cannot flow.

8.11 EFFECT OF CONCENTRATION: NERNST EQUATION

The **Nernst equation** is used to account for the effect of different activities upon electrode potential. Referring to Figure 8.14, if the Cu^{2+} ion concentration is increased with everything else remaining constant, it is readily visualized that the potential of the left electrode will become more positive because the higher concentration of electron-deficient Cu^{2+} ions clustered around it tends to draw electrons from the electrode. Decreased Cu^{2+} ion concentration has the opposite effect. If Pb^{2+} ion concentration in the right electrode is increased, it is "harder" for Pb atoms to leave the Pb electrode as positively charged ions, therefore, there is less of a tendency for electrons to be left behind on the Pb electrode, and its potential tends to be more positive. At a lower value of $[Pb^{2+}]$ in the right half-cell, the exact opposite is true. Such concentration effects upon E are expressed by the **Nernst equation**. As applied to the reaction in question,

$$Cu^{2+} + Pb \rightleftarrows Cu + Pb^{2+} \qquad E^0 = 0.463 \text{ volt} \tag{8.10.10}$$

the potential of the cell, E, is given by the Nernst equation,

$$E = E^0 + \frac{2.303RT}{nF}\log\frac{[Cu^{2+}]}{[Pb^{2+}]} = 0.463 + \underset{\substack{\uparrow \\ (\text{at } 25^\circ C)}}{\frac{0.0591}{2}}\log\frac{[Cu^{2+}]}{[Pb^{2+}]} \tag{8.11.1}$$

where R is the molar gas constant, T is the absolute temperature, *F* is the Faraday constant, n is the number of electrons involved in the half-reaction (2 in this case), and the activities are approximated by concentrations. The value of 2.303RT/*F* is 0.0591 at 25°C.

As an example of the application of the Nernst equation, suppose that $[Cu^{2+}] = 3.33 \times 10^{-4}$ mol/L and $[Pb^{2+}]$ 0.0137 mol/L. Substituting into the Nernst equation

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above gives the following:

$$E = 0.463 \text{ volt} + \frac{0.0591}{2} \log \frac{3.33 \times 10^{-4}}{0.0137} = 0.415$$

The value of E is still positive and Reaction 8.10.10 still proceeds to the right as written.

8.12 POTENTIOMETRY

Most of this discussion of electrochemistry has dealt with effects involving a flow of electrical current. It has been seen that chemical reactions can be used to produce an electrical current. It has also been seen that the flow of an electrical current through an electrochemical cell can be used to make a chemical reaction occur. Another characteristic of electricity is its voltage, or electrical potential, which was discussed as E and E^0 values above as a kind of "driving force" behind oxidation-reduction reactions.

As noted above, voltage is developed between two electrodes in an electrochemical cell. The voltage depends upon the kinds and concentrations of dissolved chemicals in the solutions contacted by the electrodes. In some cases this voltage can be used to measure concentrations of some substances in solution. This gives rise to the branch of analytical chemistry known as **potentiometry**. Potentiometry uses **ion-selective electrodes** or **measuring electrodes** whose potentials relative to a **reference electrode** vary with the concentrations of particular ions in solution. The reference electrode that serves as the ultimate standard for potentiometry is the standard hydrogen electrode shown in Figure 8.13. In practice, other electrodes, such as the silver/silver chloride or calomel (mercury metal in contact with Hg_2Cl_2) are used. A reference electrode is hooked to the reference terminal input of a voltmeter and a measuring electrode is hooked to the measuring terminal; in practice, both electrodes are immersed in the solution being analyzed and the potential of the measuring electrode is read versus the reference electrode.

Two very useful ion-selective electrodes are shown in Figure 8.15. The easier of these to understand is the fluoride ion-selective electrode consisting of a disc of lanthanum fluoride, LaF_3, molded into the end of a plastic body and connected to a wire. When this electrode is placed in solution, its potential relative to a reference electrode (an electrode whose potential does not vary with the composition of the solution) shifts more negative with increasing concentrations of F^- ion in solution. By comparing the potential of the fluoride electrode in a solution of unknown F^- concentration with its potential in a solution of known F^- concentration, it is possible to calculate the value of the unknown concentration.

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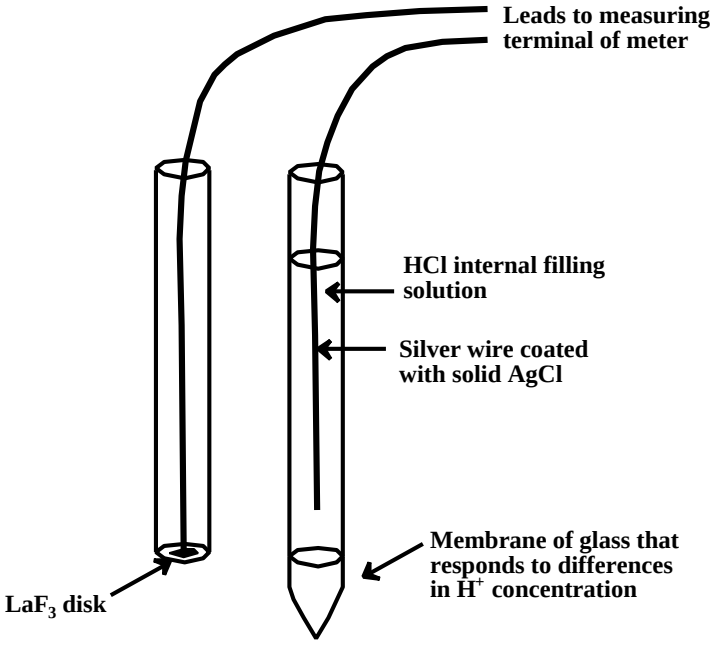


Figure 8.15 A fluoride ion-selective electrode (left) and a glass electrode used to measure pH (right).

The potential of the fluoride measuring electrode at 25˚C responds according to the Nernst equation in the form,

$$E = E_a - 0.0591 \log [F^-] \qquad (8.12.1)$$

where E is the measured potential of the fluoride electrode versus a reference electrode. (Strictly speaking, E is a function of *activity* of fluoride ion, which is approximated very well by $[F^-]$ at relatively lower concentrations of F^-.) E_a is not a true E^0, but is treated just like E^0 in the Nernst expression. Equation 8.12.1 shows that for every 10-fold increase in $[F^-]$, the potential of the fluoride electrode shifts in a negative direction by 0.0591 volt (59.1 millivolt). Increasing the concentration of a *negatively charged* ion shifts the potential to more *negative* values.

The other electrode shown in Figure 8.15 is the glass electrode used to measure H^+ concentration. Its potential varies with the concentration of H^+ ion in solution. The electrode has a special glass membrane on its end to which H^+ ions tend to adsorb. The more H^+ ions in the solution in which the electrode is dipped, the more that are adsorbed to the membrane. This adsorption of *positively charged* ions shifts the potential *positive* with increasing H^+. This shift in potential is detected by a special voltmeter with a high resistance called a **pH meter**. The pH meter makes contact with the glass membrane by way of a silver chloride (AgCl)-coated silver wire dipping into a solution of HCl contained inside the electrode. The potential is, of course, measured relative to a reference electrode, also dipping into the solution. Recall from Section 7.5 that pH is equal to the negative logarithm of the hydrogen

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ion concentration, so that as the potential of the glass electrode becomes more positive, a lower pH is indicated. The Nernst equation that applies to the glass electrode is

$$E = E_a + 0.0591 \log[H^+] \quad (8.12.2)$$

and, since $pH = -\log[H^+]$, the following applies:

$$E = E_a - 0.0591\ pH \quad (8.12.3)$$

To measure pH, the pH meter must first be calibrated. This is done by placing the electrodes in a **standard buffer solution** (a buffer solution is one that resists changes in pH with added acid, base, or water, and a standard buffer solution is one made up to an accurately known pH) of known pH. After calibration, the pH meter is then adjusted to read that pH. Next, the electrodes are removed from the buffer solution, rinsed to remove any buffer, and placed in the solution of unknown pH. This pH is then read directly from the pH meter.

8.13 CORROSION

Corrosion is defined as *the destructive alteration of metal through interactions with its surroundings*—in short, rust. It is a redox phenomenon resulting from the fact that most metals are unstable in relation to their surroundings. Thus, the steel in cars really prefers to revert back to the iron oxide ore that it came from by reacting with oxygen in the air. The corrosion process is accelerated by exposure to water, which may contain corrosive salt placed on road ice, or acid from acid rain. It is only by the application of anticorrosive coatings and careful maintenance that the process is slowed down.

Corrosion occurs when an electrochemical cell is set up on a metal surface, as shown in Figure 8.15. A layer of moisture serves to dissolve ions and act as a salt bridge between the anode and cathode. The area in which the metal is oxidized is the anode. Typically, when iron is corroded, the anode reaction is,

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^- \quad (8.13.1)$$

so that the solid iron goes into solution as Fe^{2+} ion. Several cathode reactions are possible. Usually oxygen is involved. A typical cathode reaction is

$$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O \quad (8.13.2)$$

The overall corrosion process is normally very complicated and involves a number of different reactions. Very commonly, bacteria are involved in corrosion. The bacterial cells derive energy by acting as catalysts in the corrosion reactions.

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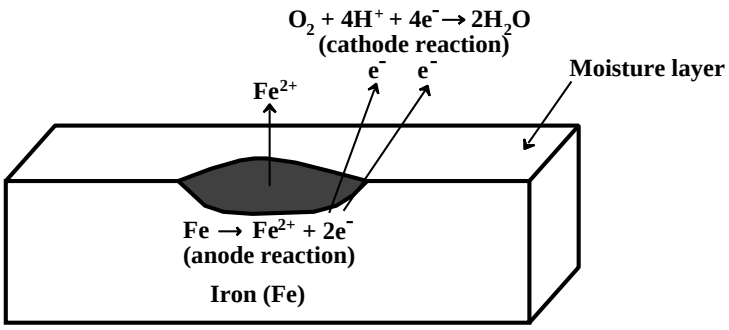


Figure 8.16 Electrochemical cell on a metal surface on which corrosion occurs.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Passing electricity through a solution of sodium sulfate in water [1]_____ _____. To a large extent, the nature of inorganic species in water depends upon whether the water is [2]_____ or [3]_____. The study of the interaction of chemistry and electricity is called [4]_____. The loss of electrons by an atom is called [5]_____, and the atom is said to have been [6]_____. A gain of electrons by an atom is called [7]_____, and the atom is said to have been [8]_____. The hypothetical charge that an atom would have if it gained or lost a particular number of electrons in forming a chemical compound is called its [9]_____. For chemically combined O the oxidation number is almost always [10]_____ and for chemically combined H it is almost always [11]_____. The oxidation number of any element in its elemental form is [12]_____. The sum of the oxidation numbers of the elements in a compound equals [13]_____, and the sum of the oxidation numbers of the elements in an ion equals [14]_____. In chemical compounds, Na, Ca, and F have oxidation numbers of [15]___, ___, and ____, respectively. When a solution containing Cu^{2+} ions comes into contact with iron metal, the products are [16]_____ _____. As a result of this process, Fe metal is [17]_____ and Cu^{2+} ion is [18]_____. A device designed to carry out a reduction half-reaction and an oxidation half-reaction in physically separate locations such that electrical energy may be extracted is called [19]_____. Metal or graphite bars that transfer electrons between wires and the solution in an electrochemical cell are called [20]_____. The one of these at which reduction occurs is called the [21]_____, and the one at which oxidation occurs is the [22]_____ _____. The function of a salt bridge is to [23]_____ _____ In a dry cell the cathode consists of [24]_____ and the anode is [25]_____. The

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overall reaction in a dry cell is [26]_____.
A reaction that is made to occur by the passage of electrical current through a solution is called [27]_____ and it takes place in [28]_____ _____. When an electrical current is passed through a solution of melted NaCl, [29]_____ is produced at the graphite anode and [30]_____ is produced at the iron cathode. When an automobile battery is discharged, [31]_____ _____ is oxidized at the anode and [32]_____ is reduced at the cathode. The device in which the overall reaction, $Cd + NiO_2 + 2H_2O \rightarrow Cd(OH)_2 + Ni(OH)_2$ occurs is the [33]_____. A device in which H_2 and O_2 are used for the direct production of electrical energy from a chemical reaction is a [34]_____. The direct conversion of light energy to electrical energy is accomplished in a [35]_____ _____. Such a device consists of two layers known as the [36]_____ and the [37]_____. The process by which electricity is used to plate a layer of metal onto an object made from another metal is called [38]_____.
In a fuel cell powered with H_2 and O_2, electrons are produced at the anode by oxidation of [39]_____ and electrons are taken up at the cathode by reduction of [40]_____. In a solar cell, doping silicon with boron atoms produces [41]_____ and doping with arsenic atoms produces [42]_____. The tendency of a half-reaction to go to the right or to the left as written is expressed by a [43]_____. Account is taken of the influence of differences in concentration on this tendency by the [44]_____. The standard electrode against which all other electrode potentials are compared is called the [45]_____ for which the assigned E^0 value is [46]_____ and the half-reaction is [47]_____. The measured potential of an electrode versus the standard hydrogen electrode when the activities of all the reaction consituents are exactly 1 is called the [48]_____ _____. The fact that the reaction $Cu^{2+} + Pb \leftarrow\rightarrow Cu + Pb^{2+}$ goes to the right as written indicates that E^0 for the half-reaction $Cu^{2+} + 2e^- \leftarrow\rightarrow Cu$ has a [49]_____ value than E^0 for the half-reaction $Pb^{2+} + 2e^- \leftarrow\rightarrow Pb$. The Nernst equation applied to the reaction $Cu^{2+} + Pb \leftarrow\rightarrow Cu + Pb^{2+}$ ($E^0 = 0.463$ volt) at 25˚C is [50]_____.
The branch of analytical chemistry in which the voltage developed by an electrode is used to measure the concentration of an ion in solution is called [51]_____. The electrodes used for this purpose are called by the general name of [52]_____ _____ and they must always be used with a [53]_____. The voltage developed at a glass membrane is used to measure [54]_____ or [55]_____. Before measurement of an unknown pH, a pH meter and its electrode system must be calibrated using a known [56]_____. The destructive alteration of metal through interactions with its surroundings is called [57]_____. In the electrochemical cell typically involved with this phenomenon, the metal is oxidized at the [58]_____.

Answers to Chapter Summary

1. breaks the water down into H_2 and O_2.
2. oxidizing

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3. reducing
4. electrochemistry
5. oxidation
6. oxidized
7. reduction
8. reduced
9. oxidation number
10. -2
11. +1
12. 0
13. 0
14. the charge on the ion
15. +1, +2, -1
16. Cu metal and Fe^{2+} ion in solution
17. oxidized
18. reduced
19. an electrochemical cell
20. electrodes
21 cathode
22. anode
23. allows for transfer of ions between half-cell
24. a graphite rod
25. A zinc cylinder
26. $2MnO_2(s) + 2NH_4^+(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + 2MnO(OH)(s) + 2NH_3(aq)$
27. an electrolytic reaction
28. an electrolytic cell
29. chlorine gas
30. liquid sodium
31. Pb metal
32. PbO_2
33. nickel-cadmium storage battery
34. fuel cell
35. solar cell
36. donor layer
37. acceptor layer
38. electroplating
39. H_2
40. O_2
41. holes
42. a donor layer
43. standard electrode potential, E^0
44. Nernst equation
45. standard hydrogen electrode, SHE
46. 0.000 volts
47. $2H^+ + 2e^- \leftarrow\rightarrow H_2$
48. standard electrode potential, E^0
49. higher
50. $E = 0.463 + 0.0591 \log [Cu^{2+}]$

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2 $[Pb^{2+}]$

51. potentiometry
52. ion-selective electrodes
53. reference electrode
54. H^+ ion concentration
55. pH
56. buffer solution
57. corrosion
58. anode

EXERCISES FOR CHAPTER 8

1. Which element has such a "strong appetite" for electrons that its name is the basis for the term used to describe loss of electrons?

2. Give the oxidation number of each of the elements marked with an asterisk in the following species: $Pb*O_2$, $N*H_4^+$, $Cl*_2$, $CaS*O_4$, $Cd*(OH)_2$

3. For what purpose is a Downs cell used?

4. How is cementation used to purify water?

5. Small mercury batteries are often used in cameras, wrist watches, and similar applications. The chemical species involved in a mercury battery are Zn, ZnO, Hg, and HgO, where Zn is the chemical symbol for zinc and Hg is that of mercury. If one were to coat a moist paste of HgO onto Zn, a reaction would occur in which Hg and Zn are produced. From this information write the cathode, anode, and overall reactions involved in the discharge of a mercury battery. You may use the oxide ion, O^{2-}, in the half-reactions.

6. What are the major ingredients of the paste used to fill a dry cell?
7. Pure water does not conduct electricity. However, by passing an electrical current through water, pure H_2 and O_2 may be prepared. What is done to the water to make this possible?

8. In this chapter, it was mentioned that Cl_2 gas could be prepared by electrolysis of a solution of NaCl in water. Elemental Na reacts with water to give NaOH and H_2 gas. Recall that the electrolysis of melted NaCl gives Na metal and Cl_2 gas. From this information, give the cathode, anode, and overall reactions for the electrolysis of a solution of NaCl in water.

9. What is the definition of cathode? What is the definition of anode?

10. Give the cathode, anode, and overall reactions when a nickel-cadmium battery is charged.

11. From a knowledge of automobile exhausts and coal-fired power plants, justify the statement that "a fuel-cell is a non-polluting source of energy."

12. What is meant by a positive hole in the acceptor layer of Si in a solar cell? What distinguishes the donor layer?

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13. From the E^0 values given in Section 8.10, give the E^0 values of the following reactions:

 (A) $2Fe^{3+} + Pb \leftarrow\rightarrow 2Fe^{2+} + Pb^{2+}$
 (B) $2Cl_2 + 2H_2O \leftarrow\rightarrow 4Cl^- + O_2 + 4H^+$
 (C) $2Ag^+ + Zn \leftarrow\rightarrow 2Ag + Zn^{2+}$
 (D) $2Fe^{3+} + Pb \leftarrow\rightarrow 2Fe^{2+} + Pb^{2+}$

14. How can it be deduced that metallic zinc and metallic lead displace H from strong acid, whereas metallic copper and silver do not?

15. Given $Fe^{3+} + e^- \leftarrow\rightarrow Fe^{2+}$, $E^0 = 0.771$ volt, and $Ce^{4+} + e^- \leftarrow\rightarrow Ce^{3+}$, $E^0 = 1.80$ volt, calculate E^0 for the reaction $Ce^{4+} + Fe^{2+} \leftarrow\rightarrow Ce^{3+} + Fe^{3+}$. Using the Nernst equation, calculate E for this reaction when $[Ce^{4+}] = 9.00 \times 10^{-3}$ mol/L, $[Ce^{3+}] = 1.25 \times 10^{-3}$ mol/L, $[Fe^{3+}] = 8.60 \times 10^{-4}$ mol/L, and $[Fe^{2+}] = 2.00 \times 10^{-2}$ mol/L.

16. In millivolts (mv) the Nernst equation (Equation 8.12.1) applied to the fluoride ion-selective electrode is $E = E_a - 59.1 \log [F^-]$. Suppose that the potential of a fluoride electrode versus a reference electrode is -88.3 mv in a solution that is 1.37×10^{-4} mol/L in F^-. What is the potential of this same electrode system in a solution for which $[F^-] = 4.68 \times 10^{-2}$ mol/L?

17. Suppose that the potential of a fluoride electrode versus a reference electrode is -61.2 mv in a solution that is 5.00×10^{-5} mol/L in F^-. What is the concentration of fluoride in a solution in which the fluoride electrode registers a potential of -18.2 volt?

18. A glass electrode has a potential of 33.3 mv versus a reference electrode in a medium for which $[H^+] = 1.13 \times 10^{-6}$ mol/L. What is the value $[H^+]$ in a solution in which the potential of the electrode registers 197.0 mv?

19. A glass electrode has a potential of 127 mv versus a reference electrode in a pH 9.03 buffer. What is the pH of a solution in which the electrode registers a potential of 195 mv?

20. Consider an electrochemical cell in which a standard hydrogen electrode is connected by way of a salt bridge to a lead electrode in contact with a Pb^{2+} solution. How does the potential of the lead electrode change when the concentration of Pb^{2+} ion is increased? Explain.

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Manahan, Stanley E. "ORGANIC CHEMISTRY"
Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

9 ORGANIC CHEMISTRY

9.1. ORGANIC CHEMISTRY

Most carbon-containing compounds are **organic chemicals** and are addressed by the subject of **organic chemistry**. Organic chemistry is a vast, diverse discipline because of the enormous number of organic compounds that exist as a consequence of the versatile bonding capabilities of carbon. Such diversity is due to the ability of carbon atoms to bond to each other through single (2 shared electrons) bonds, double (4 shared electrons) bonds, and triple (6 shared electrons) bonds in a limitless variety of straight chains, branched chains, and rings (Figure 9.1).

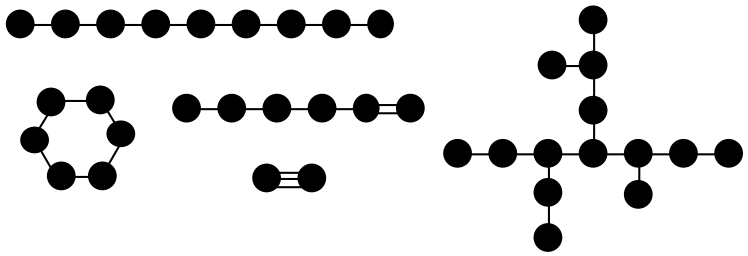


Figure 9.1 Carbon atoms in organic compounds bond with each other in straight chains, branched chains and rings. In addition to single bonds, carbon atoms may be joined by double, and even triple, bonds. Because of this remarkable bonding diversity, there are literally millions of known organic compounds.

Among organic chemicals are included the majority of important industrial compounds, synthetic polymers, agricultural chemicals, biological materials, and most substances that are of concern because of their toxicities and other hazards. Pollution of the water, air, and soil environments by organic chemicals is an area of significant concern.

Chemically, most organic compounds can be divided among hydrocarbons, oxygen-containing compounds, nitrogen-containing compounds, sulfur-containing compounds, organohalides, phosphorus-containing compounds, or combinations of

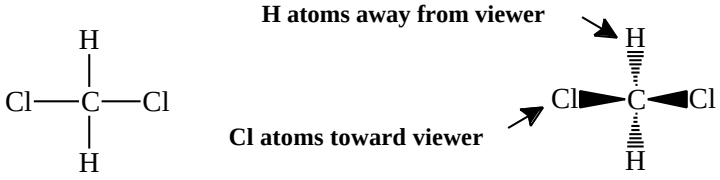
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these kinds of compounds. Each of these classes of organic compounds is discussed briefly here.

All organic compounds, of course, contain carbon. Virtually all also contain hydrogen and have at least one C–H bond. The simplest organic compounds, and those easiest to understand, are those that contain only hydrogen and carbon. These compounds are called **hydrocarbons** and are addressed first among the organic compounds discussed in this chapter. Hydrocarbons are used here to illustrate some of the most fundamental points of organic chemistry, including organic formulas, structures, and names.

Molecular Geometry in Organic Chemistry

The three-dimensional shape of a molecule, that is, its molecular geometry, is particularly important in organic chemistry. This is because its molecular geometry determines, in part, the properties of an organic molecule, particularly its interactions with biological systems and how it is metabolized by organisms. Shapes of molecules are represented in drawings by lines of normal uniform thickness for bonds in the plane of the paper; broken lines for bonds extending away from the viewer; and heavy lines for bonds extending toward the viewer. These conventions are shown by the example of dichloromethane, CH_2Cl_2, an important organochloride solvent and extractant illustrated in Figure 9.2.



Structural formula of dichloromethane in two dimensions

Representation of the three-dimensional structure of dichloromethane

Figure 9.2 Structural formulas of dichloromethane, CH_2Cl_2; the formula on the right provides a three-dimensional representation.

9.2 HYDROCARBONS

As noted above, hydrocarbon compounds contain only carbon and hydrogen. The major types of hydrocarbons are alkanes, alkenes, alkynes, and aromatic (aryl) compounds. Examples of each are shown in Figure 9.3.

Alkanes

Alkanes, also called **paraffins** or **aliphatic hydrocarbons**, are hydrocarbons in which the C atoms are joined by single covalent bonds (sigma bonds) consisting of 2 shared electrons (see Section 4.5). Some examples of alkanes are shown in Figure 9.4. As with other organic compounds, the carbon atoms in alkanes may form straight chains, branched chains, or rings. These three kinds of alkanes are, respect-

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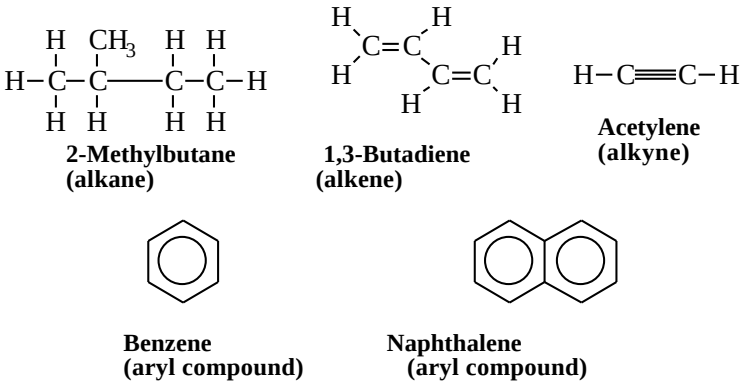


Figure 9.3 Examples of major types of hydrocarbons.

ively, **straight-chain alkanes**, **branched-chain alkanes**, and **cycloalkanes**. As shown in Figure 9.3, a typical branched-chain alkane is 2-methylbutane, a volatile, highly flammable liquid. It is a component of gasoline, which may explain why it is commonly found as an air pollutant in urban air. The general molecular formula for straight- and branched-chain alkanes is C_nH_{2n+2}, and that of cyclic alkanes is C_nH_{2n}. The four hydrocarbon molecules in Figure 9.4 contain 8 carbon atoms each. In one of the molecules, all of the carbon atoms are in a straight chain and in two they are in branched chains, whereas in a fourth, 6 of the carbon atoms are in a ring.

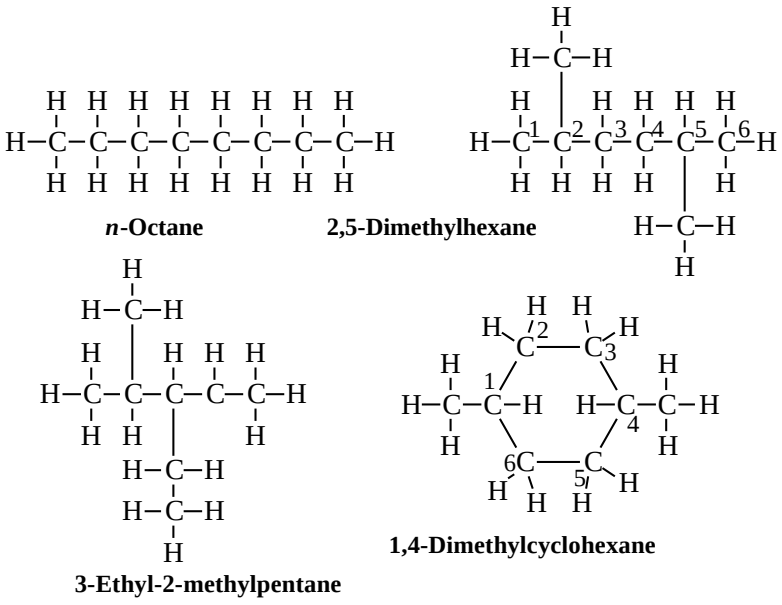


Figure 9.4 Structural formulas of four hydrocarbons, each containing 8 carbon atoms, that illustrate the structural diversity possible with organic compounds. Numbers used to denote locations of atoms for purposes of naming are shown on two of the compounds.

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Formulas of Alkanes

Formulas of organic compounds present information at several different levels of sophistication. **Molecular formulas**, such as that of octane (C_8H_{18}), give the number of each kind of atom in a molecule of a compound. As shown in Figure 9.3, however, the molecular formula of C_8H_{18} may apply to several alkanes, each one of which has unique chemical, physical, and toxicological properties. These different compounds are designated by **structural formulas** showing the order in which the atoms in a molecule are arranged. Compounds that have the same molecular but different structural formulas are called **structural isomers**. Of the compounds shown in Figure 9.4, *n*-octane, 2,5-dimethylhexane, and 3-ethyl-2-methylpentane are structural isomers, all having the formula C_8H_{18}, whereas 1,4-dimethylcyclohexane is not a structural isomer of the other three compounds because its molecular formula is C_8H_{16}.

Alkanes and Alkyl Groups

Most organic compounds can be derived from alkanes. In addition, many important parts of organic molecules contain one or more alkane groups minus a hydrogen atom bonded as substituents onto the basic organic molecule. As a consequence of these factors, the names of many organic compounds are based upon alkanes, and it is useful to know the names of some of the more common alkanes and substituent groups derived from them, as shown in Table 9.1.

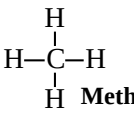
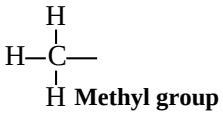
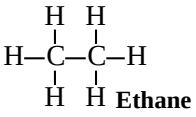
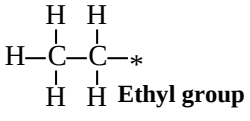
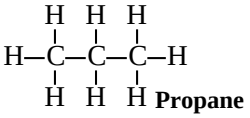
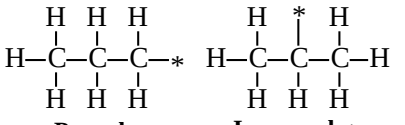
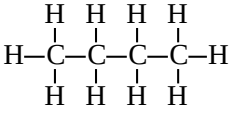
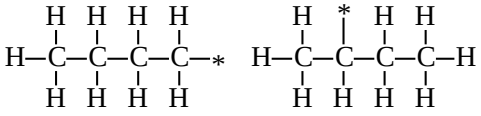
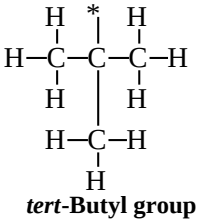
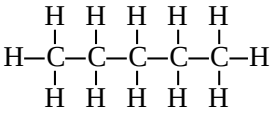
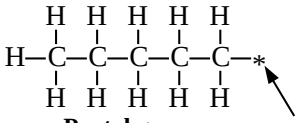
Names of Alkanes and Organic Nomenclature

Systematic names, from which the structures of organic molecules can be deduced, have been assigned to all known organic compounds. The more common organic compounds likewise have **common names** that have no structural implications. Although it is not possible to cover organic nomenclature in any detail in this chapter, the basic approach to nomenclature (naming) is presented in the chapter along with some pertinent examples. The simplest approach is to begin with names of alkane hydrocarbons.

Consider the alkanes shown in Figure 9.4. The fact that *n*-octane has no side chains is denoted by "*n*", that it has 8 carbon atoms is denoted by "oct," and that it is an alkane is indicated by "ane." The names of compounds with branched chains or atoms other than H or C attached make use of numbers that stand for positions on the longest continuous chain of carbon atoms in the molecule. This convention is illustrated by the second compound in Figure 9.4. It gets the hexane part of the name from the fact that it is an alkane with 6 carbon atoms in its longest continuous chain ("hex" stands for 6). However, it has a methyl group (CH_3) attached on the second carbon atom of the chain and another on the fifth. Hence, the full systematic name of the compound is 2,5-dimethylhexane, where "di" indicates two methyl groups. In the case of 3-ethyl-2-methylpentane, the longest continuous chain of carbon atoms contains *5* carbon atoms, denoted by *pent*ane, an ethyl group, C_2H_5, is attached to the third carbon atom, and a methyl group on the second carbon atom. The last compound shown in the figure has 6 carbon atoms in a ring, indicated by the prefix

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Table 9.1 Some Alkanes and Substituent Groups Derived from Them

Alkane	Substituent groups derived from alkane
 **Methane**	 **Methyl group**
 **Ethane**	 **Ethyl group**
 **Propane**	 ***n*-Propyl group** **Isopropyl group**
 ***n*-Butane**	 ***n*-Butyl group** ***sec*-Butyl group**
 ***tert*-Butyl group**	
 ***n*-Pentane**	 ***n*-Pentyl group** **Asterisk denotes point attachment to molecule**

"cyclo," so it is a cyclo*hex*ane compound. Furthermore, the carbon in the ring to which one of the methyl groups is attached is designated by "1" and another methyl group is attached to the fourth carbon atom around the ring. Therefore, the full name of the compound is 1,4-dimethylcyclohexane.

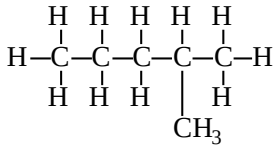
Summary of Organic Nomenclature as Applied to Alkanes

Naming relatively simple alkanes is a straightforward process. The basic rules to be followed are the following:

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1. The name of the compound is based upon the longest continuous chain of carbon atoms. (The structural formula may be drawn such that this chain is not immediately obvious.)

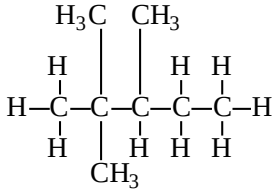
2. The carbon atoms in the longest continous chain are numbered sequentially from one end. The end of the chain from which the numbering is started is chosen to give the lower numbers for substituent groups in the final name. For example, the compound



could be named 4-methylpentane (numbering the 5-carbon chain from the left), but should be named 2-methylpentane (numbering the 5-carbon chain from the right).

3. All groups attached to the longest continuous chain are designated by the number of the carbon atoms to which they are attached and by the name of the substituent group ("2-methyl" in the example cited in Step 2 above).

4. A prefix is used to denote multiple substitutions by the same kind of group. This is illustrated by 2,2,3-trimethylpentane



in which the prefix *tri* is used to show that *three* methyl groups are attached to the pentane chain.

5. The complete name is assigned such that it denotes the longest continuous chain of carbon atoms and the name and location on this chain of each substituent group.

Reactions of Alkanes

Alkanes contain only C-C and C-H bonds, both of which are relatively strong. For that reason they have little tendency to undergo many kinds of reactions common to some other organic chemicals, such as acid-base reactions or low-temperature oxidation-reduction reactions. However, at elevated temperatures, alkanes readily undergo oxidation, more specifically combustion, with molecular oxygen in air as shown by the following reaction of propane:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O + \text{heat} \qquad (9.2.1)$$

Common alkanes are highly flammable and the more volatile lower molecular mass

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alkanes form explosive mixtures with air. Furthermore, combustion of alkanes in an oxygen-deficient atmosphere or in an automobile engine produces significant quantities of carbon monoxide, CO, the toxic properties of which are discussed in Chapter 23.

In addition to combustion, alkanes undergo **substitution reactions** in which one or more H atoms on an alkane are replaced by atoms of another element. The most common such reaction is the replacement of H by chlorine, to yield **organochlorine** compounds. For example, methane reacts with chlorine to give chloromethane. This reaction begins with the dissociation of molecular chlorine, usually initiated by ultraviolet electromagnetic radiation:

$$Cl_2 + \text{UV energy} \rightarrow Cl\cdot + Cl\cdot \quad (9.2.2)$$

The Cl· product is a **free radical** species in which the chlorine atom has only 7 outer shell electrons, as shown by the Lewis symbol,



instead of the favored octet of 8 outer-shell electrons. In gaining the octet required for chemical stability, the chlorine atom is very reactive. It abstracts a hydrogen from methane,

$$Cl\cdot + CH_4 \rightarrow HCl + CH_3\cdot \quad (9.2.3)$$

to yield HCl gas and another reactive species with an unpaired electron, $CH_3\cdot$, called methyl radical. The methyl radical attacks molecular chlorine,

$$CH_3\cdot + Cl_2 \rightarrow CH_3Cl + Cl\cdot \quad (9.2.4)$$

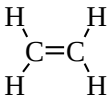
to give the chloromethane (CH_3Cl) product and regenerate Cl·, which can attack additional methane as shown in Reaction 9.7.3. The reactive Cl· and $CH_3\cdot$ species continue to cycle through the two preceding reactions.

The reaction sequence shown above illustrates three important aspects of chemistry that are shown to be very important in the discussion of atmospheric chemistry in Chapters 14–16. The first of these is that a reaction can be initiated by a **photochemical process** in which a photon of "light" (electromagnetic radiation) energy produces a reactive species, in this case the Cl· atom. The second point illustated is the high chemical reactivity of **free radical species** with unpaired electrons and incomplete octets of valence electrons. The third point illustrated is that of **chain reactions**, which can multiply manyfold the effects of a single reaction-initiating event, such as the photochemical dissociation of Cl_2.

Alkenes and Alkynes

Alkenes or olefins are hydrocarbons that have double bonds consisting of 4 shared electrons. The simplest and most widely manufactured alkene is ethylene,

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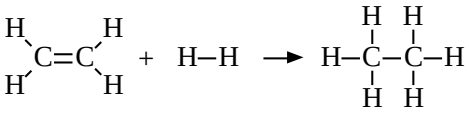
Ethylene (ethene)

used for the production of polyethylene polymer. Another example of an important alkene is 1,3-butadiene (Figure 9.3), widely used in the manufacture of polymers, particularly synthetic rubber. The lighter alkenes, including ethylene and 1,3-butadiene, are highly flammable. Like other gaseous hydrocarbons, they form explosive mixtures with air.

Acetylene (Figure 9.3) is an **alkyne**, a class of hydrocarbons characterized by carbon-carbon triple bonds consisting of 6 shared electrons. Acetylene is a highly flammable gas that forms dangerously explosive mixtures with air. It is used in large quantities as a chemical raw material. Acetylene is the fuel in oxyacetylene torches used for cutting steel and for various kinds of welding applications.

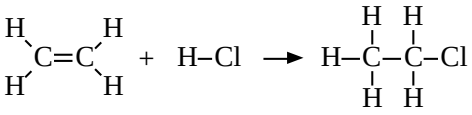
Addition Reactions

The double and triple bonds in alkenes and alkynes have "extra" electrons capable of forming additional bonds. So the carbon atoms attached to these bonds can add atoms without losing any atoms already bonded to them, and the multiple bonds are said to be **unsaturated**. Therefore, alkenes and alkynes both undergo **addition reactions** in which pairs of atoms are added across unsaturated bonds as shown in the reaction of ethylene with hydrogen to give ethane:



(9.2.5)

This is an example of a **hydrogenation reaction**, a very common reaction in organic synthesis, food processing (manufacture of hydrogenated oils), and petroleum refining. Another example of an addition reaction is that of HCl gas with acetylene to give vinyl chloride:



(9.2.6)

This kind of reaction, which is not possible with alkanes, adds to the chemical and metabolic versatility of compounds containing unsaturated bonds and is a factor contributing to their generally higher toxicities. It makes unsaturated compounds much more reactive, more hazardous to handle in industrial processes, and more active in atmospheric chemical processes such as smog formation (Chapter 16).

Alkenes and *Cis-trans* Isomerism

As shown by the two simple compounds in Figure 9.5, the two carbon atoms connected by a double bond in alkenes cannot rotate relative to each other. For this

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reason, another kind of isomerism, known as ***cis-trans*** isomerism, is possible for alkenes. *Cis-trans* isomers have different parts of the molecule oriented differently in space, although these parts occur in the same order. Both alkenes illustrated in Figure 9.5 have a molecular formula of C_4H_8. In the case of *cis*-2-butene, the two CH_3 (methyl) groups attached to the C=C carbon atoms are on the same side of the double bond, whereas in *trans*-2-butene they are on opposite sides.

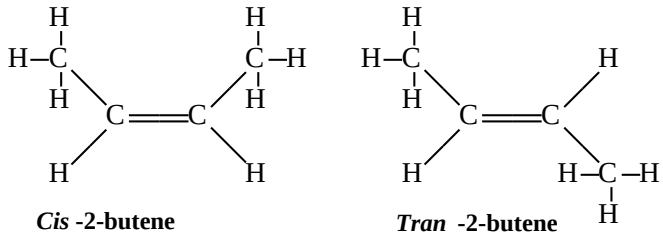


Figure 9.5. *Cis* and *trans* isomers of the alkene, 2-butene.

Condensed Structural Formulas

To save space, structural formulas are conveniently abbreviated as **condensed structural formulas** such as $CH_3CH(CH_3)CH(C_2H_5)CH_2CH_3$ for 3-ethyl-2-methylpentane, where the CH_3 (methyl) and C_2H_5 (ethyl) groups are placed in parentheses to show that they are branches attached to the longest continuous chain of carbon atoms, which contains 5 carbon atoms. It is understood that each of the methyl and ethyl groups is attached to the carbon immediately preceding it in the condensed structural formula (methyl attached to the second carbon atom, ethyl to the third).

As illustrated by the examples in Figure 9.6, the structural formulas of organic molecules can be represented in a very compact form by lines and by figures such as hexagons. The ends and intersections of straight line segments in these formulas indicate the locations of carbon atoms. Carbon atoms at the terminal ends of lines are understood to have 3 H atoms attached, C atoms at the intersections of two lines are understood to have *2* H atoms attached to each, *1* H atom is attached to a carbon represented by the intersection of three lines, and *no* hydrogen atoms are bonded to C atoms where four lines intersect. Other atoms or groups of atoms, such as the Cl atom or OH group, that are substituted for H atoms are shown by their symbols attached to a C atom with a line.

Aromatic Hydrocarbons

Benzene (Figure 9.7) is the simplest of a large class of **aromatic** or **aryl** hydrocarbons. Many important aryl compounds have substituent groups containing atoms of elements other than hydrogen and carbon and are called **aromatic compounds** or **aryl compounds**. Most aromatic compounds discussed in this book contain 6-carbon-atom benzene rings as shown for benzene, C_6H_6, in Figure 9.7. Aromatic compounds have ring structures and are held together in part by particularly stable bonds that contain delocalized clouds of so-called π (pi, pronounced “pie”) electrons.

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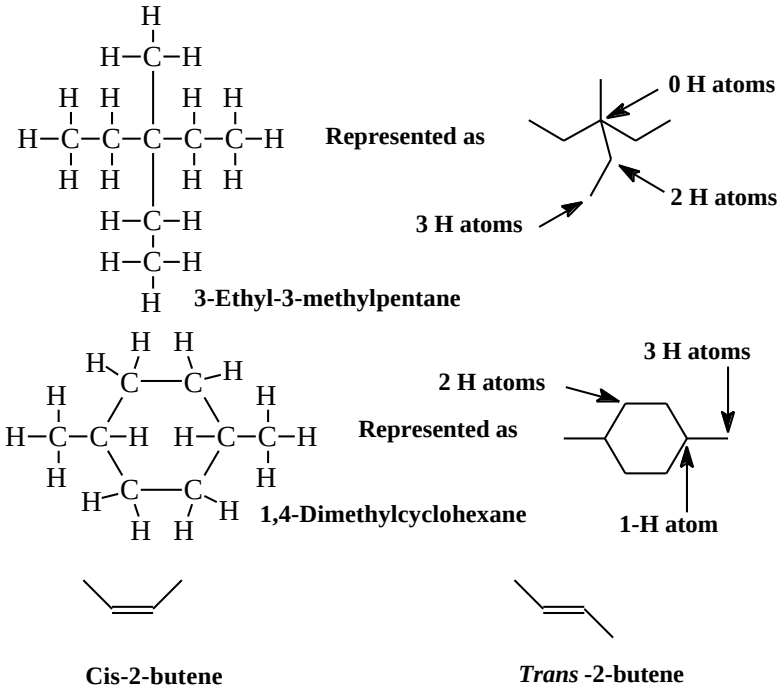


Figure 9.6 Representation of structural formulas with lines. A carbon atom is understood to be at each corner and at the end of each line. The numbers of hydrogen atoms attached to carbons at several specific locations are shown with arrows.

In an oversimplified sense, the structure of benzene can be visualized as resonating between the two equivalent structures shown on the left in Figure 9.7 by the shifting of electrons in chemical bonds to form a hybrid structure. This structure can be shown more simply and accurately by a hexagon with a circle in it.

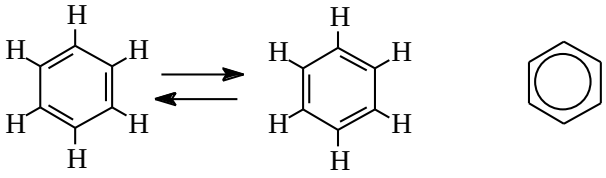


Figure 9.7 Representation of the aromatic benzene molecule with two resonance structures (left) and, more accurately, as a hexagon with a circle in it (right). Unless shown by symbols of other atoms, it is understood that a C atom is at each corner and that 1 H atom is bonded to each C atom.

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Aromatic compounds have special characteristics of **aromaticity**, which include a low hydrogen:carbon atomic ratio; C–C bonds that are quite strong and of intermediate length between such bonds in alkanes and those in alkenes; tendency to undergo substitution reactions rather than the addition reactions characteristic of alkenes; and delocalization of π electrons over several carbon atoms. The last phenomenon adds substantial stability to aromatic compounds and is known as **resonance stabilization**.

Benzene, toluene, and other lighter aromatic compounds were first isolated from hydrocarbon liquids produced as a byproduct of coal coking, a process in which the coal is heated in the absence of air to produce a carbonaceous residue used in steel-making. Now recovered during the refining of crude oil, these aromatic liquid compounds have found widespread use as solvents, in chemical synthesis, and as a fuel. Many toxic substances, environmental pollutants, and hazardous waste compounds, such as benzene, naphthalene, and chlorinated phenols, are aromatic compounds (see Figure 9.8). As shown in Figure 9.8, some arenes, such as naphthalene and the polycyclic aromatic compound, benzo(a)pyrene, contain fused rings.

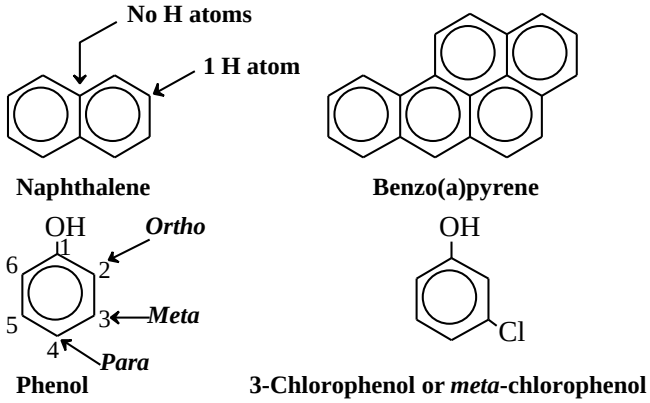


Figure 9.8 Aromatic compounds containing fused rings (top) and showing the numbering of carbon atoms for purposes of nomenclature.

Benzene and Naphthalene

Benzene is a volatile, colorless, highly flammable liquid used to manufacture phenolic and polyester resins, polystyrene plastics, alkylbenzene surfactants, chlorobenzenes, insecticides, and dyes. It is hazardous both for its ignitability and toxicity (exposure to benzene causes blood abnormalities that may develop into leukemia). Naphthalene is the simplest member of a large number of polycyclic (multicyclic) aromatic hydrocarbons having two or more fused rings. It is a volatile white crystalline solid with a characteristic odor and has been used to make moth-balls. The most important of the many chemical derivatives made from naphthalene is phthalic anhydride, from which phthalate ester plasticizers are synthesized.

Polycyclic Aromatic Hydrocarbons

Benzo(a)pyrene (Figure 9.8) is the most studied of the polycyclic aromatic hydrocarbons (PAHs), which are characterized by condensed ring systems (“chicken

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wire" structures). These compounds are formed by the incomplete combustion of other hydrocarbons, a process that consumes hydrogen in preference to carbon. The carbon residue is left in the thermodynamically favored condensed aromatic ring system of the PAH compounds.

Because there are so many partial combustion and pyrolysis processes that favor production of PAHs, these compounds are encountered abundantly in the atmosphere, soil, and elsewhere in the environment from sources that include engine exhausts, wood stove smoke, cigarette smoke, and charbroiled food. Coal tars and petroleum residues such as road and roofing asphalt have high levels of PAHs. Some PAH compounds, of which the most widely investigated has been the 5-ringed compound benzo(a)pyrene, are of toxicological concern because they are precursors to cancer-causing metabolites.

9.3. ORGANIC FUNCTIONAL GROUPS AND CLASSES OF ORGANIC COMPOUNDS

The discussion of organic chemistry so far in this chapter has emphasized hydrocarbon compounds, those that contain only hydrogen and carbon. It has been shown that hydrocarbons may exist as alkanes, alkenes, and arenes, depending upon the kinds of bonds between carbon atoms. The presence of elements other than hydrogen and carbon in organic molecules greatly increases the diversity of their chemical properties. As shown in Table 9.2, **functional groups** consist of specific bonding configurations of atoms in organic molecules. Most functional groups contain at least one element other than carbon or hydrogen, although 2 carbon atoms joined by a double bond (alkenes) or triple bond (alkynes) are likewise considered to be functional groups. Table 9.2 shows some of the major functional groups that determine the nature of organic compounds.

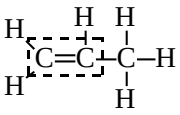
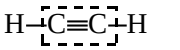
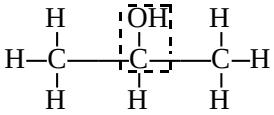
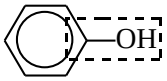
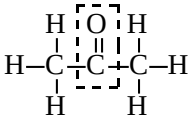
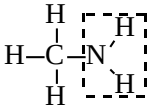
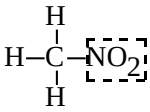
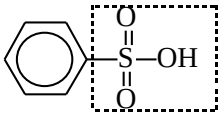
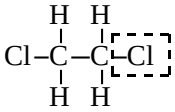
Organooxygen Compounds

The most common types of compounds with oxygen-containing functional groups are epoxides, alcohols, phenols, ethers, aldehydes, ketones, and carboxylic acids. The functional groups characteristic of these compounds are illustrated by the examples of oxygen-containing compounds shown in Figure 9.9.

Ethylene oxide is a moderately to highly toxic, sweet-smelling, colorless, flammable, explosive gas used as a chemical intermediate, sterilant, and fumigant. It is a mutagen and a carcinogen to experimental animals. It is classified as hazardous for both its toxicity and ignitability. **Methanol** is a clear, volatile, flammable liquid alcohol used for chemical synthesis, as a solvent, and as a fuel. It is used as a gasoline additive to reduce emissions of carbon monoxide and other air pollutants. Ingestion of methanol can be fatal, and blindness can result from sublethal doses. **Phenol** is a dangerously toxic aromatic alcohol widely used for chemical synthesis and polymer manufacture. **Methyltertiarybutyl ether**, MTBE, is an ether that became the octane booster of choice to replace tetraethyllead in gasoline. However, in 1999 both the State of California and the U. S. Environmental Protection Agency proposed phasing it out, largely because of concern over its water pollution potential.

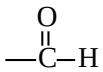
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Table 9.2 Examples of Some Important Functional Groups

Type of functional group	Example compound	Structural formula of group[1]
Alkene (olefin)	Propene (propylene)	
Alkyne	Acetylene	
Alcohol (-OH attached to alkyl group)	2-Propanol	
Phenol (-OH attached to aryl group)	Phenol	
Ketone (When  group is on end carbon, compound is an aldehyde)	Acetone	
Amine	Methylamine	
Nitro compounds	Nitromethane	
Sulfonic acids	Benzenesulfonic acid	
Organohalides	1,1–Dichloro-ethane	

[1] Functional group outlined by dashed line

Acrolein is an alkenic aldehyde and a volatile, flammable, highly reactive chemical. It forms explosive peroxides upon prolonged contact with O_2. An extreme lachrimator and strong irritant, acrolein is quite toxic by all routes of exposure. **Acetone** is the lightest of the ketones. Like all ketones, acetone has a carbonyl (C=O) group that is bonded to *2* carbon atoms (that is, it is somewhere in the middle of a carbon atom chain). Acetone is a good solvent and is chemically less reactive than the aldehydes, which all have the functional group



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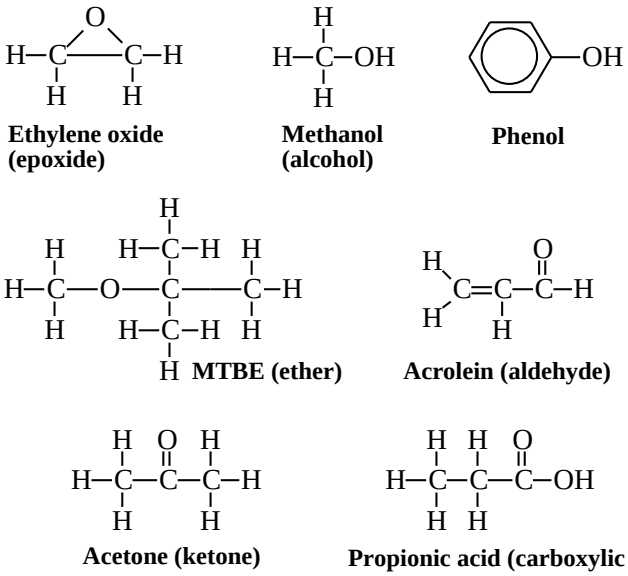


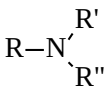
Figure 9.9 Examples of oxygen-containing organic compounds that may be significant as wastes, toxic substances, or environmental pollutants.

in which binding of the C=O to H makes the molecule significantly more reactive. **Propionic acid** is a typical organic carboxylic acid. The $-CO_2H$ group of carboxylic acids may be viewed as the most oxidized functional group (other than peroxides) on an oxygenated organic compound, and carboxylic acids can be synthesized by oxidizing alcohols or aldehydes that have an -OH group or C=O group on an end carbon atom.

Organonitrogen Compounds

Figure 9.10 shows examples of three classes of the many kinds of compounds that contain N (amines, nitrosamines, and nitro compounds). Nitrogen occurs in many functional groups in organic compounds, some of which contain nitrogen in ring structures, or along with oxygen.

Methylamine is a colorless, highly flammable gas with a strong odor. It is a severe irritant affecting eyes, skin, and mucous membranes. Methylamine is the simplest of the **amine** compounds, which have the general formula



where the Rs are hydrogen or hydrocarbon groups, at least one of which is the latter.

Dimethylnitrosamine is one of the N-nitroso compounds, all characterized by the N-N=O functional group. It was once widely used as an industrial solvent, but caused liver damage and jaundice in exposed workers. Subsequently, numerous other N-nitroso compounds, many produced as byproducts of industrial operations and food and alcoholic beverage processing, were found to be carcinogenic.

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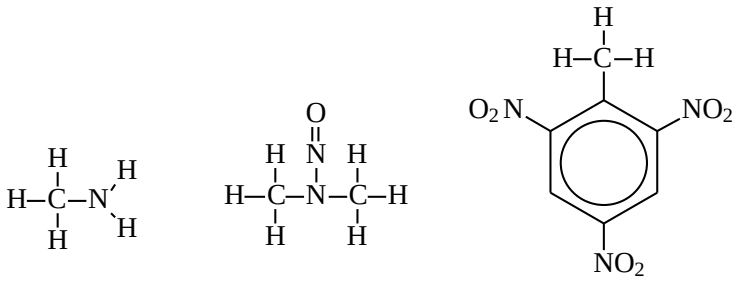
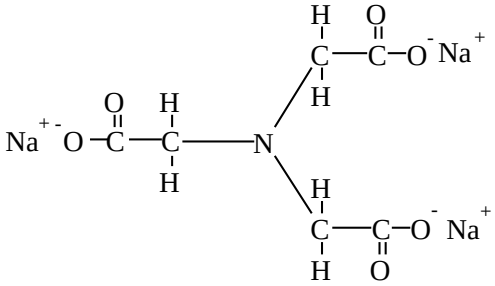


Figure 9.10 Examples of organonitrogen that may be significant as wastes, toxic substances, or environmental pollutants.

Solid **2,4,6-trinitrotoluene** (TNT) has been widely used as a military explosive. TNT is moderately to very toxic and has caused toxic hepatitis or aplastic anemia in exposed individuals, a few of whom have died from its toxic effects. It belongs to the general class of nitro compounds characterized by the presence of $-NO_2$ groups bonded to a hydrocarbon structure.

Some organonitrogen compounds are chelating agents that bind strongly to metal ions and play a role in the solubilization and transport of heavy metal wastes. Prominent among these are salts of the aminocarboxylic acids which, in the acid form, have $-CH_2CO_2H$ groups bonded to nitrogen atoms. An important example of such a compound is the monohydrate of trisodium nitrilotriacetate (NTA):



This compound can be used as a substitute for detergent phosphates to bind to calcium ion and make the detergent solution basic. NTA is used in metal plating formulations. It is highly water soluble and quickly eliminated with urine when ingested. It has a low acute toxicity and no chronic effects have been shown for plausible doses. However, concern does exist over its interaction with heavy metals in waste-treatment processes and in the environment.

Organohalide Compounds

Organohalides (Figure 9.11) exhibit a wide range of physical and chemical properties. These compounds consist of halogen-substituted hydrocarbon molecules, each of which contains at least one atom of F, Cl, Br, or I. They may be saturated (**alkyl halides**), unsaturated (**alkenyl halides**), or aromatic (**aromatic halides**). The

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most widely manufactured organohalide compounds are chlorinated hydrocarbons, many of which are regarded as environmental pollutants or as hazardous wastes.

Alkyl Halides

Substitution of halogen atoms for one or more hydrogen atoms on alkanes gives **alkyl halides**, example structural formulas of which are given in Figure 9.11. Most of the commercially important alkyl halides are derivatives of alkanes of low molecular mass. A brief discussion of the uses of the compounds listed in Figure 9.11 is given here to provide an idea of the versatility of the alkyl halides.

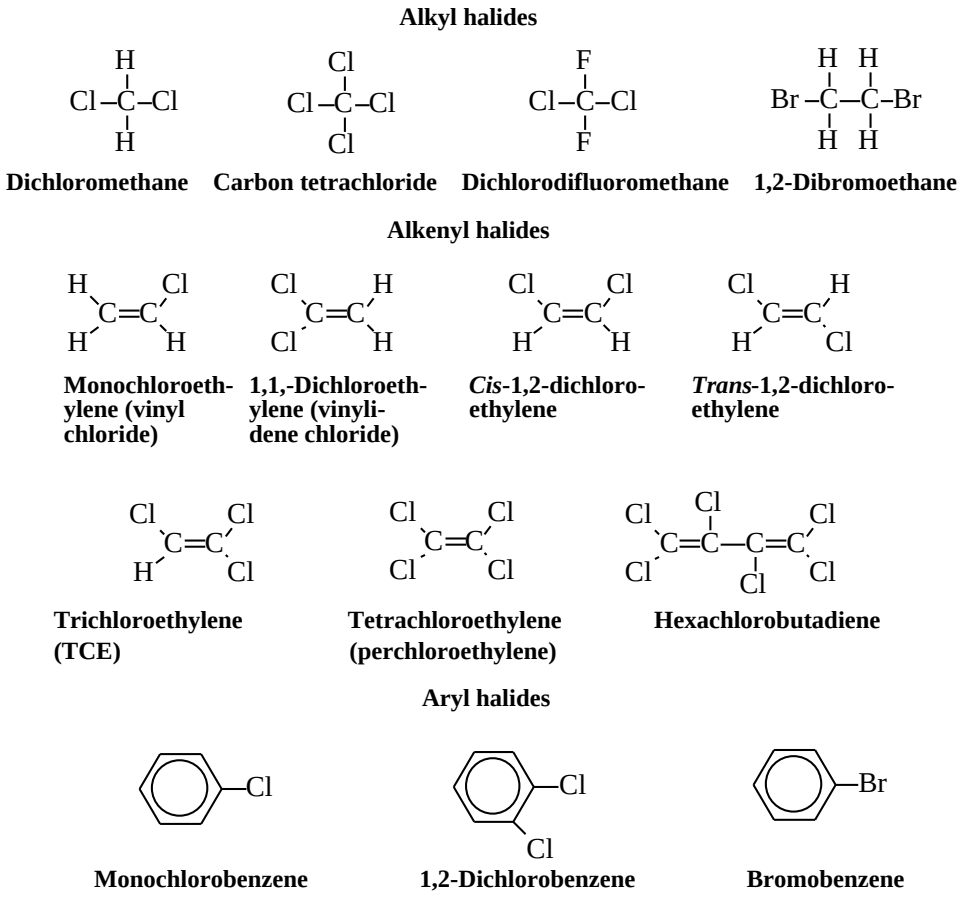


Figure 9.11 Examples of organohalide compounds.

Dichloromethane is a volatile liquid with excellent solvent properties for non-polar organic solutes. It has been used as a solvent for the decaffeination of coffee, in paint strippers, as a blowing agent in urethane polymer manufacture, and to depress vapor pressure in aerosol formulations. Once commonly sold as a solvent and stain remover, highly toxic **carbon tetrachloride** is now largely restricted to uses as a chemical intermediate under controlled conditions, primarily to manufacture

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chlorofluorocarbon refrigerant fluid compounds, which are also discussed in this section. Insecticidal **1,2-dibromoethane** has been consumed in large quantities as a lead scavenger in leaded gasoline and to fumigate soil, grain, and fruit (fumigation with this compound has been discontinued because of toxicological concerns). An effective solvent for resins, gums, and waxes, it serves as a chemical intermediate in the synthesis of some pharmaceutical compounds and dyes.

Alkenyl Halides

Viewed as hydrocarbon-substituted derivatives of alkenes, the **alkenyl** or **olefinic organohalides** contain at least 1 halogen atom and at least 1 carbon-carbon double bond. The most significant of these, which are materials produced in large quantities for chemical manufacture and other purposes, are the lighter chlorinated compounds, such as those illustrated in Figure 9.11.

Vinyl chloride is consumed in large quantities as a raw material to manufacture pipe, hose, wrapping, and other products fabricated from polyvinylchloride plastic. This highly flammable, volatile, sweet-smelling gas is a known human carcinogen.

As shown in Figure 9.11, there are three possible dichloroethylene compounds, all clear, colorless liquids. Vinylidene chloride forms a copolymer with vinyl chloride used in some kinds of coating materials. The geometrically isomeric 1,2-dichloroethylenes are used as organic synthesis intermediates and as solvents. **Trichloroethylene** is a clear, colorless, nonflammable, volatile liquid. It is an excellent degreasing and drycleaning solvent and has been used as a household solvent and for food extraction (for example, in decaffeination of coffee). Colorless, nonflammable liquid **tetrachloroethylene** has properties and uses similar to those of trichloroethylene. **Hexachlorobutadiene**, a colorless liquid with an odor somewhat like that of turpentine, is used as a solvent for higher hydrocarbons and elastomers, as a hydraulic fluid, in transformers, and for heat transfer.

Aromatic Halides

Aromatic halide derivatives of benzene and toluene have many uses. They are common intermediates and raw materials in chemical synthesis. In addition, they are used as pesticides and raw materials for pesticides manufacture, as solvents, and for a diverse variety of other applications. These widespread uses over many decades have resulted in substantial human exposure and environmental contamination. Three example aromatic halides are shown in Figure 9.11. Monochlorobenzene is a flammable liquid boiling at 132˚C. It is used as a solvent, heat transfer fluid, and synthetic reagent. Used as a solvent, 1,2-dichlorobenzene is employed for degreasing hides and wool. It also serves as a synthetic reagent for dye manufacture. Bromobenzene is a liquid boiling at 156˚C that is used as a solvent, motor oil additive, and intermediate for organic synthesis.

Halogenated Naphthalene and Biphenyl

Two major classes of halogenated aromatic compounds containing 2 benzene rings are made by the chlorination of naphthalene and biphenyl and have been sold

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as mixtures with varying degrees of chlorine content. Examples of chlorinated naphthalenes, and polychlorinated biphenyls (PCBs discussed later), are shown in Figure 9.12. The less highly chlorinated of these compounds are liquids, and those with higher chlorine contents are solids. Because of their physical and chemical stabilities and other qualities, these compounds have had many uses, including heat transfer fluids, hydraulic fluids, and dielectrics. Polybrominated biphenyls (PBBs) have served as flame retardants. However, because chlorinated naphthalenes, PCBs, and PBBs are extremely persistent, their uses have been severely curtailed.

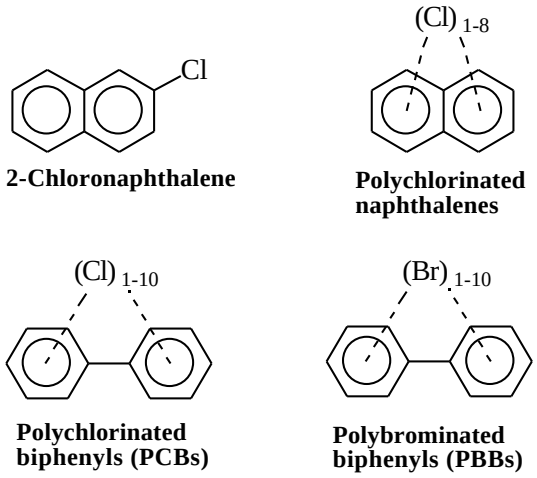


Figure 9.12 Halogenated naphthalenes and biphenyls.

Chlorofluorocarbons, Halons, and Hydrogen-Containing Chlorofluorocarbons

Chlorofluorocarbons (**CFC**s) are volatile 1- and 2-carbon compounds that contain Cl and F bonded to carbon. These extremely stable and nontoxic compounds are discussed in some detail in Section 16.4. They were once widely used in the fabrication of flexible and rigid foams, and as fluids for refrigeration and air conditioning, but have now been essentially phased out because of their potential to cause harm to the stratospheric ozone layer. The most widely manufactured of these compounds in the past were CCl_3F (CFC-11), CCl_2F_2 (CFC-12), $C_2Cl_3F_3$ (CFC-113), $C_2Cl_2F_4$ (CFC-114), and C_2ClF_5 (CFC-115). **Halons** are related compounds that contain bromine and are used in fire extinguisher systems. The most commonly produced commercial halons were $CBrClF_2$ (Halon-1211), $CBrF_3$ (Halon-1301), and $C_2Br_2F_4$ (Halon-2402), where the sequence of numbers denotes the number of carbon, fluorine, chlorine, and bromine atoms, respectively, per molecule. Halons have also been implicated as ozone-destroying gases in the stratosphere and are being phased out. However, finding suitable replacements has been difficult, particularly in the crucial area of aircraft fire extinguishers.

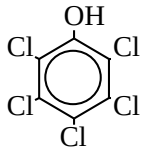
Hydrohalocarbons are hydrogen-containing chlorofluorocarbons (HCFCs) and hydrogen-containing fluorocarbons (HFCs) that are now produced as substitutes for chlorofluorocarbons. These compounds include CH_2FCF_3 (HFC-134a, a substitute

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for CFC-12 in automobile air conditioners and refrigeration equipment), $CHCl_2CF_3$ (HCFC-123, substitute for CFC-11 in plastic foam-blowing), CH_3CCl_2F (HCFC-141b, substitute for CFC-11 in plastic foam-blowing), and $CHClF_2$ (HCFC-22, air conditioners and manufacture of plastic foam food containers). Because each molecule of these compounds has at least one H-C bond, which is much more readily broken than C-Cl or C-F bonds, the HCFCs do not persist in the atmosphere and pose essentially no threat to the stratospheric ozone layer.

Chlorinated Phenols

The chlorinated phenols, particularly **pentachlorophenol** and the trichlorophenol isomers, are significant hazardous wastes. These compounds are biocides that are used to treat wood to prevent rot by fungi and to prevent termite infestation. They are toxic, causing liver malfunction and dermatitis. However, contaminant polychlorinated dibenzodioxins ("dioxin") may be responsible for some of the observed effects. Pentachlorophenol and other aromatic halides and aromatic hydrocarbons used as wood preservatives are encountered at many hazardous-waste sites in wastewaters and sludges.



Pentachlorophenol

Organosulfur Compounds

The chemistry of sulfur is similar to but perhaps more diverse than that of oxygen. Whereas, with the exception of peroxides, most chemically combined organic oxygen is in the -2 oxidation state, sulfur occurs in the -2, +4, and +6 oxidation states. Many organosulfur compounds are noted for their "rotten egg" or garlic odors. A number of example organosulfur compounds are shown in Figure 9.13.

Substitution of alkyl or aromatic hydrocarbon groups such as phenyl and methyl for H on hydrogen sulfide, H_2S, leads to a number of different organosulfur **thiols** (mercaptans, R–SH) and **sulfides**, also called thioethers (R–S–R). Structural formulas of examples of these compounds are shown in Figure 9.13.

Methanethiol and other lighter alkyl thiols are fairly common air pollutants that have "ultragarlic" odors; both 1- and 2-butanethiol are associated with skunk odor. Gaseous methanethiol is used as an odorant leak-detecting additive for natural gas, propane, and butane; it is also employed as an intermediate in pesticide synthesis. A toxic, irritating volatile liquid with a strong garlic odor, 2-propene-1-thiol (allyl mercaptan) is a typical alkenyl mercaptan. Benzenethiol (phenyl mercaptan) is the simplest of the aromatic thiols. It is a toxic liquid with a severely "repulsive" odor.

Alkyl sulfides or thioethers contain the C-S-C functional group. The lightest of these compounds is dimethyl sulfide, a volatile liquid (bp 38˚C) that is moderately toxic by ingestion. It is now known to be a major source of gaseous sulfur entering the atmosphere over the oceans due to its production by marine organisms. Cyclic sulfides contain the C-S-C group in a ring structure. The most common of these com-

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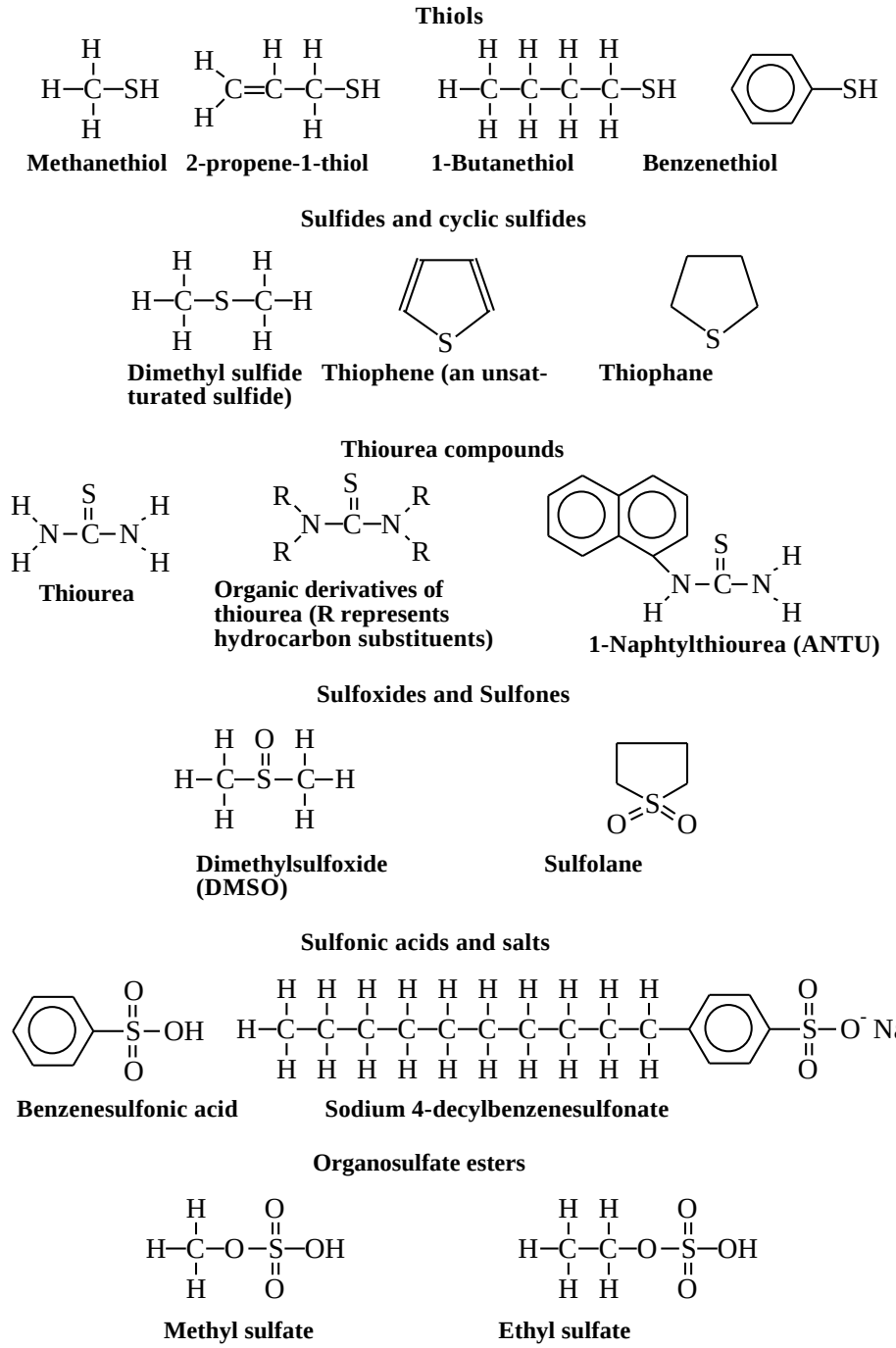


Figure 9.13 Examples of organosulfur compounds.

pounds is thiophene, a heat-stable liquid (bp 84˚C) with a solvent action much like that of benzene, that is used to make pharmaceuticals, dyes, and resins. Its saturated analog is tetrahydrothiophene, or thiophane.

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Many important organosulfur compounds also contain nitrogen. One such compound is **thiourea**, the sulfur analog of urea. Its structural formula is shown in Figure 9.13. Thiourea and **phenylthiourea** have been used as rodenticides. Commonly called ANTU, **1-naphthylthiourea** is an excellent rodenticide that is virtually tasteless and has a very high rodent:human toxicity ratio.

Sulfoxides and **sulfones** (Figure 9.13) contain both sulfur and oxygen. **Dimethylsulfoxide** (DMSO) is a liquid used to remove paint and varnish, as a hydraulic fluid, mixed with water as an antifreeze solution, and in pharmaceutical applications as an anti-inflammatory and bacteriostatic agent. **Sulfolane** dissolves both organic and inorganic solutes and is widely used in BTX processing to selectively extract benzene, toluene, and xylene from aliphatic hydrocarbons; as the solvent in the Sulfinol process by which thiols and acidic compounds are removed from natural gas; as a solvent for polymerization reactions; and as a polymer plasticizer.

Sulfonic acids and sulfonate salts contain the $-SO_3H$ and $-SO_3^-$ groups, respectively, attached to a hydrocarbon moiety. The structural formula of benzenesulfonic acids and of sodium 4-decylbenzenesulfonate, a biodegradable detergent surfactant, are shown in Figure 9.13. The common sulfonic acids are water-soluble strong acids that lose virtually all ionizable H^+ in aqueous solution. They are used commercially to hydrolyze fat and oil esters to fatty acids and glycerol.

Replacement of 1 H on sulfuric acid, H_2SO_4, with a hydrocarbon group yields an acid ester, and replacement of both yields an ester, examples of which are shown in Figure 9.13. Sulfuric acid esters are used as alkylating agents, which act to attach alkyl groups (such as methyl) to organic molecules in the manufacture of agricultural chemicals, dyes, and drugs. **Methylsulfuric acid** and **ethylsulfuric acid** are oily, water-soluble liquids that are strong irritants to skin, eyes, and mucous tissue.

Organophosphorus Compounds

The first two examples in Figure 9.14, illustrate that the structural formulas of alkyl and aromatic phosphine compounds can be derived by substituting organic groups for the H atoms in phosphine (PH_3), the toxic hydride of phosphorus. **Methylphosphine** is a colorless, reactive gas. Crystalline, solid **triphenylphosphine** has a low reactivity and moderate toxicity when inhaled or ingested.

As shown by the reaction,

$$4C_3H_9P + 26O_2 \rightarrow 12CO_2 + 18H_2O + P_4O_{10} \qquad (9.3.1)$$

combustion of aromatic and alkyl phosphines produces P_4O_{10}, a corrosive, irritant, toxic substance that reacts with moisture in the air to produce droplets of corrosive orthophosphoric acid, H_3PO_4.

The structural formulas of three common esters of orthophosphoric acid (H_3PO_4) and an ester of pyrophosphoric acid ($H_4P_2O_6$) are shown in Figure 9.14. Although **trimethylphosphate** is considered to be only moderately toxic, **tri-*o*-cresylphosphate**, **TOCP,** has a notorious record of poisonings. **Tetraethylpyrophosphate**, **TEPP**, was developed in Germany during World War II as a substitute for insecticidal nicotine. Although it is a very effective insecticide, its use in that application was of very short duration because it kills almost everything else, too.

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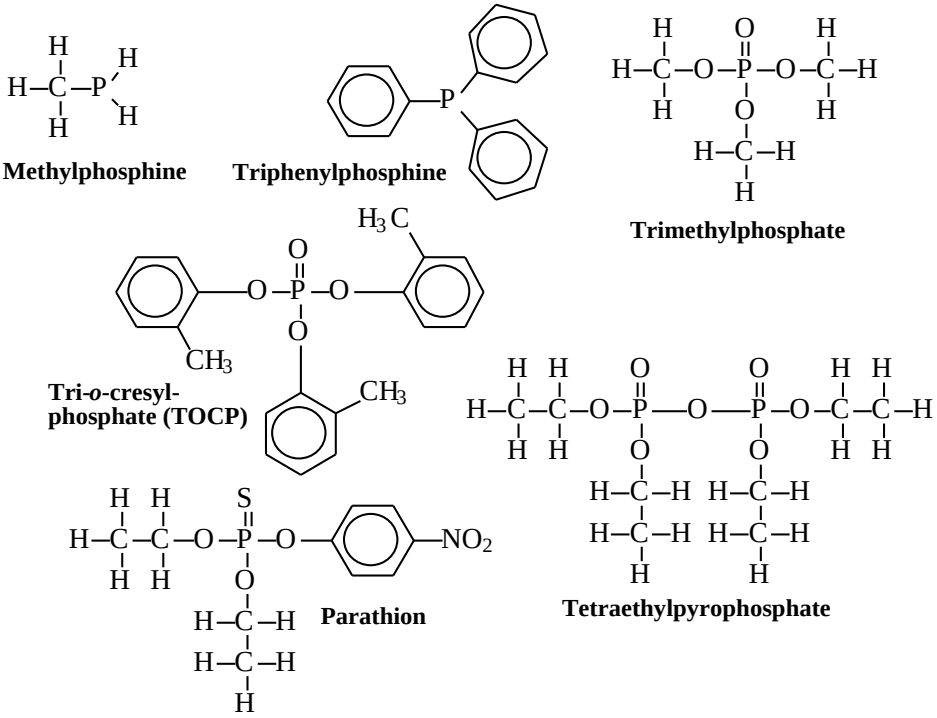


Figure 9.14 Some representative organophosphorus compounds.

Phosphorothionate Esters

Parathion, shown in Figure 9.14, is an example of **phosphorothionate** esters. These compounds are used as insecticidal acetylcholinesterase inhibitors. They contain the P=S (thiono) group, which increases their insect:mammal toxicity ratios. Since the first organophosphate insecticides were developed in Germany during the 1930s and 1940s, many insecticidal organophosphate compounds have been synthesized. One of the earliest and most successful of these is **parathion**, *O*,*O*-diethyl-*O*-*p*-nitrophenylphosphorothionate (banned from use in the U.S. in 1991 because of its acute toxicity to humans). From a long-term environmental standpoint, organophosphate insecticides are superior to the organohalide insecticides that they largely displaced because the organophosphates readily undergo biodegradation and do not bioaccumulate.

9.4 SYNTHETIC POLYMERS

The huge polymer manufacture industry is significant to the environment both as a source of environmental pollutants and in the manufacture of materials used to alleviate environmental and waste problems. Synthetic **polymers** are produced when small molecules called **monomers** bond together to form a much smaller number of very large molecules. Many natural products are polymers; for example, cellulose produced by trees and other plants and found in wood, paper, and many other mater-

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ials, is a polymer of the sugar glucose. Synthetic polymers form the basis of many industries, such as rubber, plastics, and textiles manufacture.

An important example of a polymer is that of polyvinylchloride, shown in Figure 9.15. This polymer is synthesized in large quantities for the manufacture of water and sewer pipe, water-repellant liners, and other plastic materials. Other major polymers include polyethylene (plastic bags, milk cartons), polypropylene, (impact-resistant plastics, indoor-outdoor carpeting), polyacrylonitrile (Orlon, carpets), polystyrene (foam insulation), and polytetrafluoroethylene (Teflon coatings, bearings); the monomers from which these substances are made are shown in Figure 9.16.

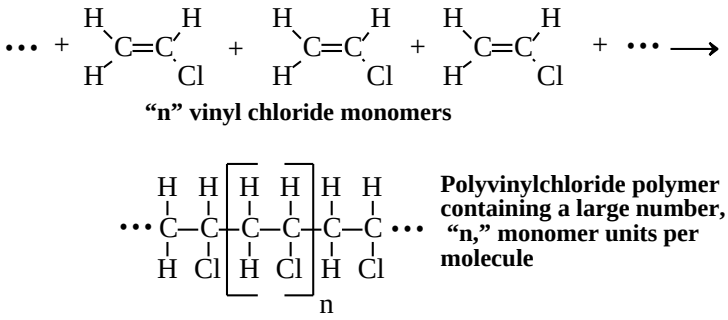


Figure 9.15 Polyvinylchloride polymer.

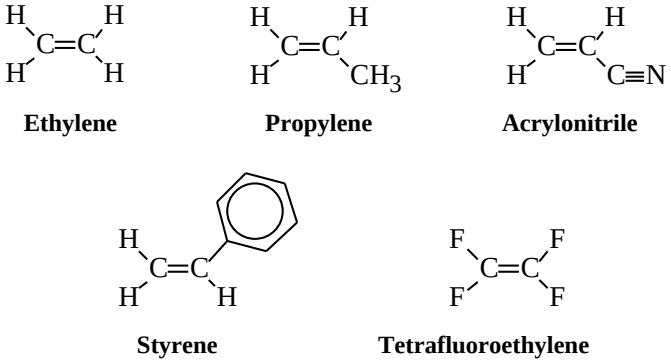


Figure 9.16 Monomers from which commonly used polymers are synthesized.

Many of the hazards from the polymer industry arise from the monomers used as raw materials. Many monomers are reactive and flammable, with a tendency to form explosive vapor mixtures with air. All have a certain degree of toxicity; vinyl chloride is a known human carcinogen. The combustion of many polymers may result in the evolution of toxic gases, such as hydrogen cyanide (HCN) from polyacrylonitrile, or hydrogen chloride (HCl) from polyvinylchloride. Another hazard presented by plastics results from the presence of **plasticizers** added to provide essential properties such as flexibility. The most widely used plasticizers are phthalates, which are environmentally persistent, resistant to treatment processes, and prone to undergo bioaccumulation.

Polymers have a number of applications in waste treatment and disposal. Waste disposal landfill liners are made from synthetic polymers, as are the fiber filters that remove particulate pollutants from flue gas in baghouses. Membranes used for

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ultrafiltration and reverse osmosis treatment of water are composed of very thin sheets of synthetic polymers. Organic solutes can be removed from water by sorption onto hydrophobic (water-repelling) organophilic beads of Amberlite XAD resin. Heavy metal pollutants are removed from wastewater by cation exchange resins made of polymers with anionic functional groups. Typically, these resins exchange harmless sodium ion, Na^+, on the solid resin for toxic heavy metal ions in water. Figure 9.17 shows a segment of the polymeric structure of a cation exchange

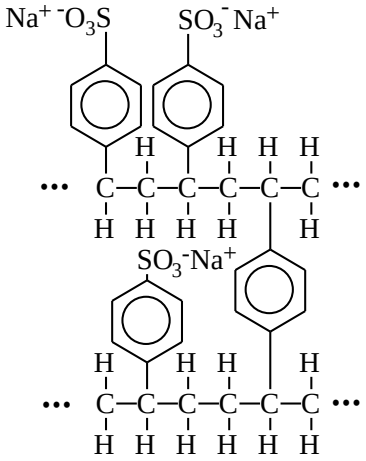


Figure 9.17 Polymeric cation exchanger in the sodium form.

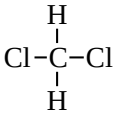
resin in the sodium form. In the treatment of heavy-metal-containing waste solutions, these resins can exchange toxic heavy metal ions in solution, such as Cd^{2+}, for nontoxic Na^+ ions. Ion exchange resins are used in nuclear reactors to remove traces of metals, some of which may be radioactive, from the water used in the reactor for heat exchange. Ion exchange resins have also been developed in which the ion-exchanging functional group is an iminiodiacetate $\{-N(CH_2CO_2^-)_2\}$ group that has a particularly strong affinity for heavy metals.

CHAPTER SUMMARY

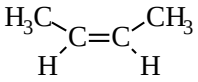
The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Organic chemistry is so diverse because of the ability of carbon atoms to bond to each other through [1]_____, _____, and _____, bonds in a huge variety of [2]_____. All organic compounds contain [3]_____ and most contain the element [4]_____. Although represented on paper by structures such as,

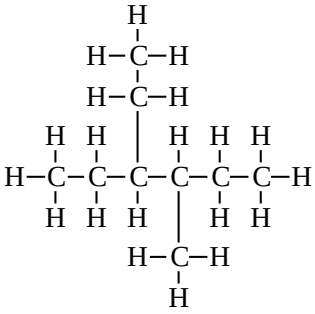
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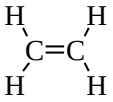
the [5]_____ of organic molecules is particularly important in determining their behavior. The simplest class of organic compounds containing only two elements are the [6]_____ divided into the four general classes of [7]_____. Hydrocarbons with a general formula such as C_8H_{18} may exist as a variety of different [8]_____ _____. The compound



has a "twin" compound with the same molecular formula, the two of which compose a pair of [9]_____. The systematic name of the compound

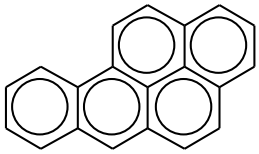


is [10]_____ and its condensed structural formula is [11]_____ _____ The systematic name of an organic compound is based upon the [12]_____ chain of carbon atoms. The two most common reactions of alkanes are [13]_____. A free radical is [14]_____ _____ one of which may be formed intially by a [15]_____ process. The compound,



Ethylene (ethene)

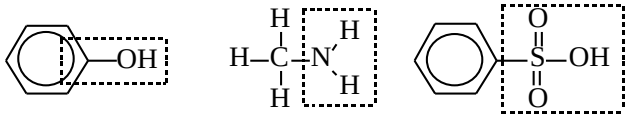
is an example of an [16]_____ hydrocarbon These compounds undergo [17]____ _____ reactions that cannot occur with alkanes. Hydrocarbons containing the 6-membered ring C_6H_6 or derivatives of it are examples of [18]_____. The compound



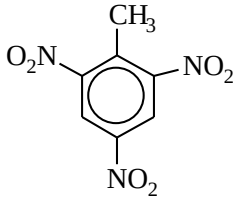
belongs to the class of [19]_____, some of which

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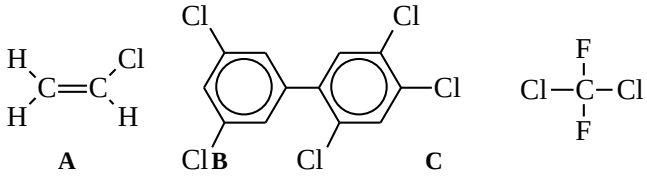
are of concern because [20]_____.
Groups such as those outlined by dashed rectangles below are called [21]_____



_____. The structural formula of the functional group characteristic of aldehydes is [22]_____ and that characteristic of carboxylic acids is [23]_____. Amines are characterized by [24]_____ _____. The compound

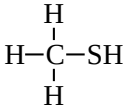


is called [25]_____ and is used as an [26]_____.
Organohalide compounds are those that contain [27]_____. Of the compounds



A **B** **C**

"A" is of concern because it is [28]_____, "B" because it is [29]_____, and "C" because it [30]_____ _____. The compound,

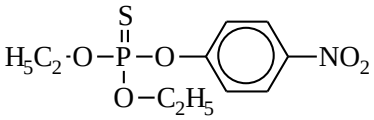


is an example of a [31]_____, a class of organosulfur compounds noted for their [32]_____. Sulfonic acids contain the [33]_____ group. Phosphorothionate esters such as parathion, for which the structural formula is [34]_____ are effective as insecticides because they [35]_____. Synthetic polymers are formed when small [36]_____ molecules join together to form [37]_____ _____.

Answers to Chapter Summary

1. single, double, triple
2. straight chains, branched chains, and rings
3. carbon
4. hydrogen

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5. molecular geometry
6. hydrocarbons
7. alkanes, alkenes, alkynes, and aromatic hydrocarbons
8. structural isomers that have different arrangements of atoms
9. *cis-trans* isomers
10. 3-ethyl-4-methylhexane
11. $CH_3CH_2CH(C_2H_5)CH(CH_3)CH_2CH_3$
12. longest continuous
13. oxidation (combustion) and substitution reactions
14. a species with an unpaired electron, such as Cl·
15. photochemical
16. alkene
17. addition
18. aromatic or aryl hydrocarbons
19. polycyclic aromatic hydrocarbons
20. they may cause cancer
21. functional groups
22. 
23. 
24. A nitrogen atom bonded to at least one hydrocarbon group and that may be bonded to 1 or 2 H atoms
25. 2,4,6-trinitrotoluene
26. explosive
27. F, Cl, Br, or I
28. a known human carcinogen
29. environmentally persistent
30. depletes stratospheric ozone
31. thiol compound
32. bad odors
33. 
34. 
35. inhibit acetylcholinesterase
36. monomer
37. very large molecules

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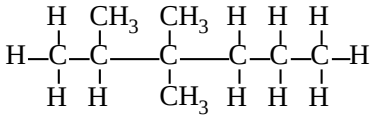
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QUESTIONS AND PROBLEMS

1. Explain the bonding properties of carbon that make organic chemistry so diverse.
2. Distinguish among alkanes, alkenes, alkynes, and aromatic compounds. To which general class of organic compounds do all belong?
3. In what sense are alkanes saturated? Why are alkenes more reactive than alkanes?

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4. Name the compound below:



5. What is indicated by "*n*" in a hydrocarbon name?
6. Discuss the chemical reactivity of alkanes. Why are they chemically reactive or unreactive?
7. Discuss the chemical reactivity of alkenes. Why are they chemically reactive or unreactive?
8. What are the characteristics of aromaticity? What are the chemical reactivity characteristics of aromatic compounds?
9. Describe chain reactions, discussing what is meant by free radicals and photochemical processes.
10. Define, with examples, what is meant by isomerism.
11. Describe how the two forms of 1,2-dichloroethylene can be used to illustrate *cis-trans* isomerism.
12. Give the structural formula corresponding to the condensed structural formula of $CH_3CH(C_2H_5)CH(C_2H_5)CH_2CH_3$.
13. Discuss how organic functional groups are used to define classes of organic compounds.
14. Give the functional groups corresponding to (a) alcohols, (b) aldehydes, (c) carboxylic acids, (d) ketones, (e) amines, (f) thiol compounds, and (g) nitro compounds.
15. Give an example compound of each of the following: epoxides, alcohols, phenols, ethers, aldehydes, ketones, and carboxylic acids.
16. Which functional group is characteristic of N-nitroso compounds, and why are these compounds toxicologically significant?
17. Give an example of each of the following: Alkyl halides, alkenyl halides, aromatic halides.
18. Give an example compound of a chlorinated naphthalene and of a PCB.
19. What explains the tremendous chemical stability of CFCs? What kinds of compounds are replacing CFCs? Why?
20. How does a thio differ from a thioether?
21. How do sulfoxides differ from sulfones?

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22. Which inorganic compound is regarded as the parent compound of alkyl and aromatic phosphines? Give an example of each of these.
23. What are organophosphate esters and what is their toxicological significance?
24. Define what is meant by a polymer and give an example of one.

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10 BIOLOGICAL CHEMISTRY

10.1 BIOCHEMISTRY

Most people have had the experience of looking through a microscope at a single cell. It may have been an ameba, alive and oozing about like a blob of jelly on the microscope slide, or a cell of bacteria, stained with a dye to make it show up more plainly. Or, it may have been a beautiful cell of algae with its bright green chlorophyll. Even the simplest of these cells is capable of carrying out a thousand or more chemical reactions. These life processes fall under the heading of **biochemistry**, that branch of chemistry that deals with the chemical properties, composition, and biologically mediated processes of complex substances in living systems.

Biochemical phenomena that occur in living organisms are extremely sophisticated. In the human body, complex metabolic processes break down a variety of food materials to simpler chemicals, yielding energy and the raw materials to build body constituents such as muscle, blood, and brain tissue. Impressive as this may be, consider a humble microscopic cell of photosynthetic cyanobacteria only about a micrometer in size, which requires only a few simple inorganic chemicals and sunlight for its existence. This cell uses sunlight energy to convert carbon from CO_2, hydrogen and oxygen from H_2O, nitrogen from NO_3^-, sulfur from SO_4^{2-}, and phosphorus from inorganic phosphate into all the proteins, nucleic acids, carbohydrates, and other materials that it requires to exist and reproduce. Such a simple cell accomplishes what could not be done by human endeavors even in a vast chemical factory costing billions of dollars.

Ultimately, most environmental pollutants and hazardous substances are of concern because of their effects upon living organisms. The study of the adverse effects of substances on life processes requires some basic knowledge of biochemistry. Biochemistry is discussed in this chapter, with emphasis upon aspects that are especially pertinent to environmentally hazardous and toxic substances, including cell membranes, DNA, and enzymes.

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Biochemical processes not only are profoundly influenced by chemical species in the environment, they largely determine the nature of these species, their degradation, and even their syntheses, particularly in the aquatic and soil environments. The study of such phenomena forms the basis of **environmental biochemistry**.[1]

Biomolecules

The biomolecules that constitute matter in living organisms are often polymers with molecular masses of the order of a million or even larger. As discussed later in this chapter, these biomolecules can be divided into the categories of carbohydrates, proteins, lipids, and nucleic acids. Proteins and nucleic acids consist of macromolecules, lipids are usually relatively small molecules, and carbohydrates range from relatively small sugar molecules to high molecular mass macromolecules such as those in cellulose.

The behavior of a substance in a biological system depends to a large extent upon whether the substance is hydrophilic ("water-loving") or hydrophobic ("water-hating"). Some important toxic substances are hydrophobic, a characteristic that enables them to traverse cell membranes readily. Part of the detoxification process carried on by living organisms is to render such molecules hydrophilic, therefore water-soluble and readily eliminated from the body.

10.2 BIOCHEMISTRY AND THE CELL

The focal point of biochemistry and biochemical aspects of toxicants is the **cell**, the basic building block of living systems where most life processes are carried out. Bacteria, yeasts, and some algae consist of single cells. However, most living things are made up of many cells. In a more complicated organism, the cells have different functions. Liver cells, muscle cells, brain cells, and skin cells in the human body are quite different from each other and do different things. Cells are divided into two major categories depending upon whether they have a nucleus: **eukaryotic** cells have a nucleus and **prokaryotic** cells do not. Prokaryotic cells are found in single-celled bacteria. Eukaryotic cells compose organisms other than bacteria.

Major Cell Features

Figure 10.1 shows the major features of the **eukaryotic cell**, which is the basic structure in which biochemical processes occur in multicelled organisms. These features are the following:

- **Cell membrane**, which encloses the cell and regulates the passage of ions, nutrients, lipid-soluble ("fat-soluble") substances, metabolic products, toxicants, and toxicant metabolites into and out of the cell interior because of its varying **permeability** for different substances. The cell membrane protects the contents of the cell from undesirable outside influences. Cell membranes are composed in part of phospholipids that are arranged with their hydrophilic ("water-seeking") heads on the cell membrane surfaces and their hydrophobic ("water-repelling") tails inside the membrane. Cell membranes contain bodies of proteins that are involved in the transport of

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some substances through the membrane. One reason the cell membrane is very important in toxicology and environmental biochemistry is that it regulates the passage of toxicants and their products into and out of the cell interior. Furthermore, when its membrane is damaged by toxic substances, a cell may not function properly and the organism may be harmed.

- **Cell nucleus**, which acts as a sort of "control center" of the cell. It contains the genetic directions the cell needs to reproduce itself. The key substance in the nucleus is **deoxyribonucleic** acid (**DNA**). **Chromosomes** in the cell nucleus are made up of combinations of DNA and proteins. Each chromosome stores a separate quantity of genetic information. Human cells contain 46 chromosomes. When DNA in the nucleus is damaged by foreign substances, various toxic effects, including mutations, cancer, birth defects, and defective immune system function may occur.

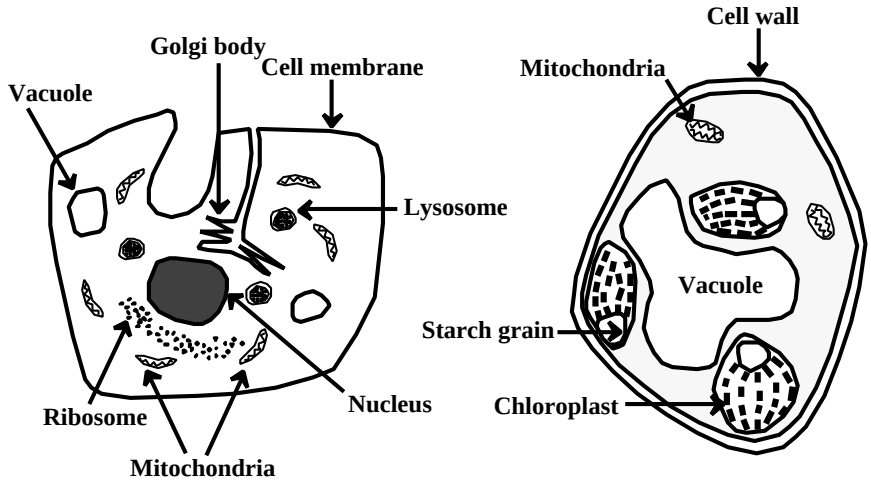


Figure 10.1 Some major features of the eukaryotic cell in animals (left) and plants (right).

- **Cytoplasm**, which fills the interior of the cell not occupied by the nucleus. Cytoplasm is further divided into a water-soluble proteinaceous filler called **cytosol**, in which are suspended bodies called **cellular organelles**, such as mitochondria or, in photosynthetic organisms, chloroplasts.
- **Mitochondria**, "powerhouses," which mediate energy conversion and utilization in the cell. Mitochondria are sites in which food materials—carbohydrates, proteins, and fats—are broken down to yield carbon dioxide, water, and energy, which is then used by the cell for its energy needs. The best example of this is the oxidation of the sugar glucose, $C_6H_{12}O_6$:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy}$$

This kind of process is called **cellular respiration.**

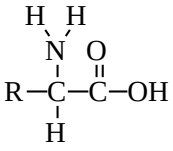
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- **Ribosomes**, which participate in protein synthesis.
- **Endoplasmic reticulum**, which is involved in the metabolism of some toxicants by enzymatic processes.
- **Lysosome**, a type of organelle that contains potent substances capable of digesting liquid food material. Such material enters the cell through a "dent" in the cell wall, which eventually becomes surrounded by cell material. This surrounded material is called a **food vacuole**. The vacuole merges with a lysosome, and the substances in the lysosome bring about digestion of the food material. The digestion process consists largely of **hydrolysis reactions** in which large, complicated food molecules are broken down into smaller units by the addition of water.
- **Golgi bodies**, which occur in some types of cells, flattened bodies of material that serve to hold and release substances produced by the cells.
- **Cell walls** of plant cells. These are strong structures that provide stiffness and strength. Cell walls are composed mostly of cellulose, which will be discussed later in this chapter.
- **Vacuoles** inside plant cells that often contain materials dissolved in water.
- **Chloroplasts** in plant cells that are involved in photosynthesis (the chemical process that uses energy from sunlight to convert carbon dioxide and water to organic matter). Photosynthesis occurs in these bodies. Food produced by photosynthesis is stored in the chloroplasts in the form of **starch grains**.

10.3 PROTEINS

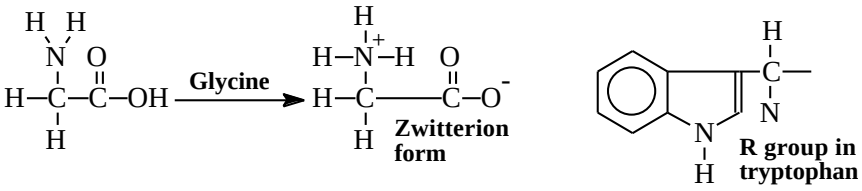
Proteins are nitrogen-containing organic compounds that are the basic units of live systems. Cytoplasm, the jelly-like liquid filling the interior of cells, is made up largely of protein. Enzymes, which act as catalysts of life reactions, are made of proteins; they are discussed later in the chapter. Proteins are made up of **amino acids** joined together in huge chains. Amino acids are organic compounds that contain the carboxylic acid group, $-CO_2H$, and the amino group, $-NH_2$. They are sort of a hybrid of carboxylic acids and amines (See Chapter 9). Proteins are polymers or **macromolecules** of amino acids containing from approximately 40 to several thousand amino acid groups joined by peptide linkages. Smaller molecule amino acid polymers, containing only about 10 to about 40 amino acids per molecule, are called **polypeptides**. A portion of the amino acid left after the elimination of H_2O during polymerization is called a **residue**. The amino acid sequence of these residues is designated by a series of three-letter abbreviations for the amino acid.

Natural amino acids all have the following chemical group:



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In this structure, the $-NH_2$ group is always bonded to the carbon next to the $-CO_2H$ group. This is called the "alpha" location, so natural amino acids are alpha-amino acids. Other groups, designated as "R," are attached to the basic alpha-amino acid structure. The R groups may be as simple as an atom of H found in glycine,



or, they may be as complicated as the structure of the R group in tryptophan. As shown in Figure 10.2, there are 20 common amino acids in proteins. These are shown with uncharged $-NH_2$ and $-CO_2H$ groups. Actually, these functional groups exist in the charged **zwitterion** form as shown for glycine above.

Amino acids in proteins are joined together in a specific way. These bonds constitute the **peptide linkage**. The formation of peptide linkages is a condensation process involving the loss of water. Consider, as an example, the condensation of alanine, leucine, and tyrosine shown in Figure 10.3. When these three amino acids join together, two water molecules are eliminated. The product is a *tri*peptide since there are three amino acids involved. The amino acids in proteins are linked as shown for this tripeptide, except that many more monomeric amino acid groups are involved.

Proteins may be divided into several major types that have widely varying functions. These are listed in Table 10.1.

Protein Structure

The order of amino acids in protein molecules, and the resulting three-dimensional structures that form, provide an enormous variety of possibilities for **protein structure**. This is what makes life so diverse. Proteins have primary, secondary, tertiary, and quaternary structures. The structures of protein molecules determine the behavior of proteins in crucial areas such as the processes by which the body's immune system recognizes substances that are foreign to the body. Proteinaceous enzymes depend upon their structures for the very specific functions of the enzymes.

The order of amino acids in the protein molecule determines its *primary structure*. **Secondary protein structures** result from the folding of polypeptide protein chains to produce a maximum number of hydrogen bonds between peptide linkages:

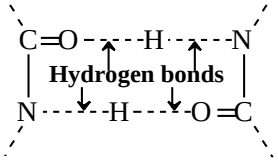


Illustration of hydrogen bonds between N and O atoms in peptide linkages, which constitute protein secondary structures

Further folding of the protein molecules held in place by attractive forces between amino acid side chains is determined by the nature of the amino acid R groups.

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Small R groups enable protein molecules to be hydrogen-bonded together in a parallel arrangement whereas larger R groups produce a spiral form known as an **alpha-helix**.

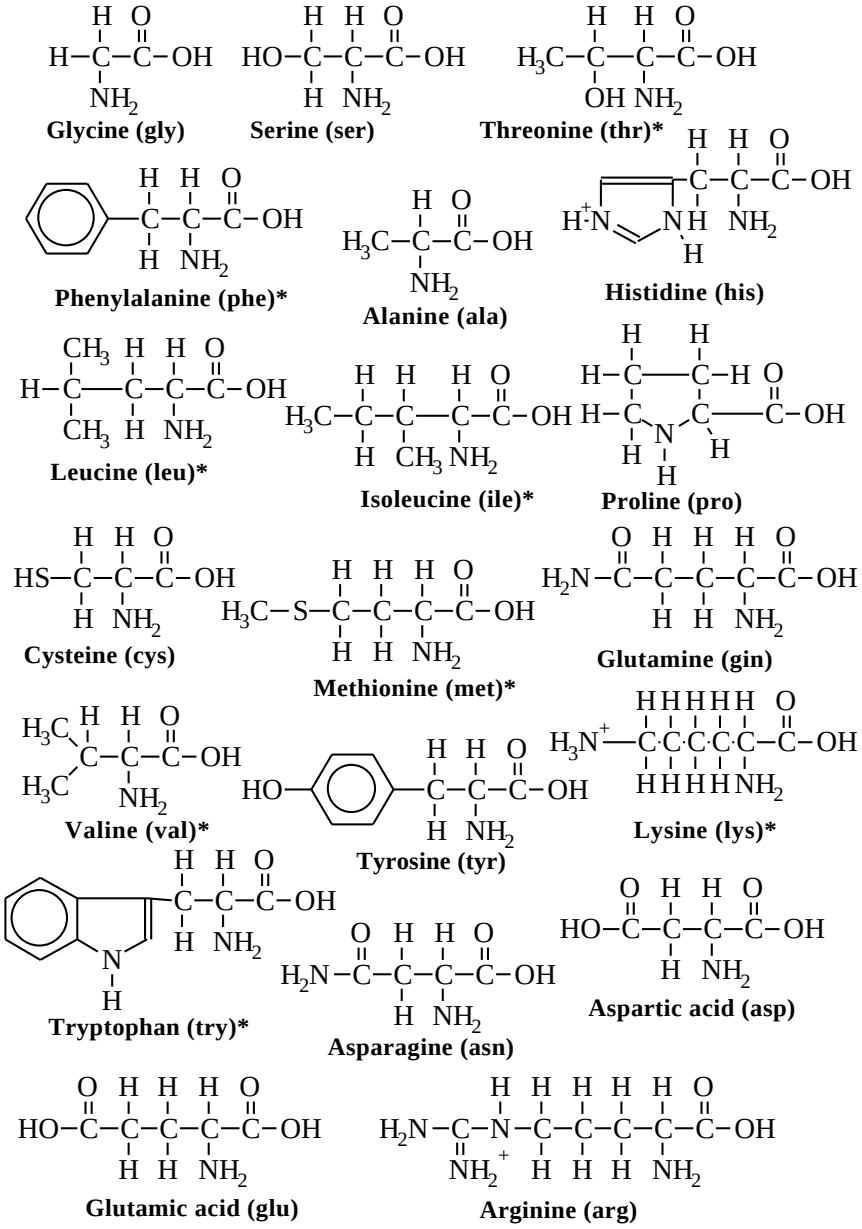


Figure 10.2 Amino acids that occur in proteins. Those marked with an asterisk cannot be synthesized by the human body and must come from dietary sources.

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Table 10.1 Major Types of Proteins

Type of protein	Example	Function and characteristics
Nutrient	Casein (milk protein)	Food source. People must have an adequate supply of nutrient protein with the right balance of amino acids for adequate nutrition.
Storage	Ferritin	Storage of iron in animal tissues
Structural	Collagen (tendons) keratin (hair)	Structural and protective components in organisms
Contractile	Actin, myosin in muscle tissue	Strong, fibrous proteins that can contract and cause movement to occur
Transport	Hemoglobin	Transport inorganic and organic species across cell membranes, in blood, between organs
Defense	- - -	Antibodies against foreign agents such as viruses produced by the immune system
Regulatory	Insulin, human growth hormone	Regulate biochemical processes such as sugar metabolism or growth by binding to sites inside cells or on cell membranes
Enzymes	Acetylcholin-esterase	Catalysts of biochemical reactions (see Section 10.6.)

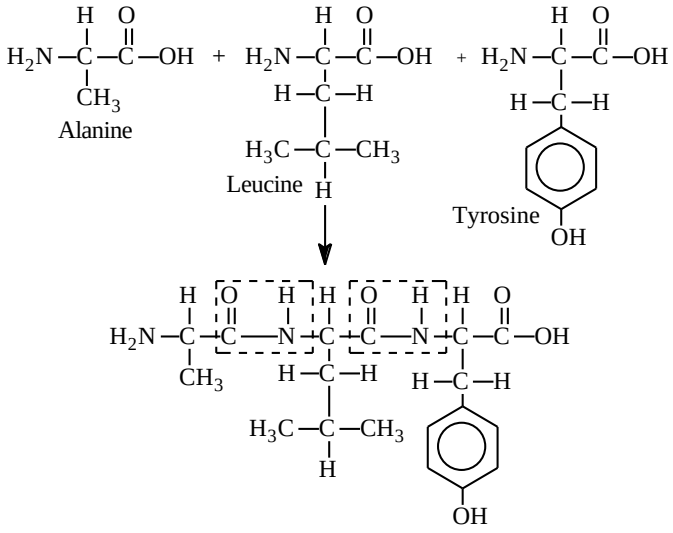


Figure 10.3 Condensation of alanine, leucine, and tyrosine to form a tripeptide consisting of three amino acids joined by peptide linkages (outlined by dashed lines).

Tertiary structures are formed by the twisting of alpha-helices into specific shapes. They are produced and held in place by the interactions of amino side chains on the amino acid residues constituting the protein macromolecules. Tertiary protein

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structure is very important in the processes by which enzymes identify specific proteins and other molecules upon which they act. It is also involved with the action of antibodies in blood that recognize foreign proteins by their shape and react to them. This is what happens in the phenomenon of disease immunity where antibodies in blood recognize specific proteins from viruses or bacteria and reject them.

Two or more protein molecules consisting of separate polypeptide chains may be further attracted to each other to produce a **quaternary structure**.

Some proteins are **fibrous proteins**, which occur in skin, hair, wool, feathers, silk, and tendons. The molecules in these proteins are long and threadlike and are laid out parallel in bundles. Fibrous proteins are quite tough and they do not dissolve in water.

An interesting fibrous protein is keratin, which is found in hair. The cross-linking bonds between protein molecules in keratin are –S–S– bonds formed from two HS– groups in two molecules of the amino acid, cysteine. These bonds largely hold hair in place, thus keeping it curly or straight. A "permanent" consists of breaking the bonds chemically, setting the hair as desired, then reforming the cross-links to hold the desired shape.

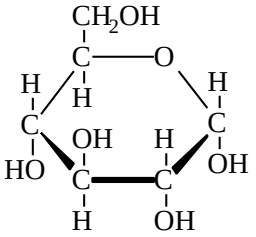
Aside from fibrous protein, the other major type of protein form is the **globular protein**. These proteins are in the shape of balls and oblongs. Globular proteins are relatively soluble in water. A typical globular protein is hemoglobin, the oxygen-carrying protein in red blood cells. Enzymes are generally globular proteins.

Denaturation of Proteins

Secondary, tertiary, and quaternary protein structures are easily changed by a process called **denaturation**. These changes can be quite damaging. Heating, exposure to acids or bases, and even violent physical action can cause denaturation to occur. The albumin protein in egg white is denatured by heating so that it forms a semisolid mass. Almost the same thing is accomplished by the violent physical action of an egg beater in the preparation of meringue. Heavy metal poisons such as lead and cadmium change the structures of proteins by binding to functional groups on the protein surface.

10.4 CARBOHYDRATES

Carbohydrates have the approximate simple formula CH_2O and include a diverse range of substances composed of simple sugars such as glucose:



Glucose molecule

High-molecular-mass **polysaccharides**, such as starch and glycogen ("animal starch"), are biopolymers of simple sugars.

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Photosynthesis in a plant cell converts the energy from sunlight to chemical energy in a carbohydrate, $C_6H_{12}O_6$. This carbohydrate may be transferred to some other part of the plant for use as an energy source. It may be converted to a water-insoluble carbohydrate for storage until it is needed for energy. Or it may be transformed to cell wall material and become part of the structure of the plant. If the plant is eaten by an animal, the carbohydrate is used for energy by the animal.

The simplest carbohydrates are the **monosaccharides**. These are also called **simple sugars**. Because they have 6 carbon atoms, simple sugars are sometimes called *hex*oses. Glucose (formula shown above) is the most common simple sugar involved in cell processes. Other simple sugars with the same formula but somewhat different structures are fructose, mannose, and galactose. These must be changed to glucose before they can be used in a cell. Because of its use for energy in body processes, glucose is found in the blood. Normal levels are from 65 to 110 mg glucose per 100 ml of blood. Higher levels may indicate diabetes.

Units of two monosaccharides make up several very important sugars known as **disaccharides**. When two molecules of monosaccharides join together to form a disaccharide,

$$C_6H_{12}O_6 + C_6H_{12}O_6 \rightarrow C_{12}H_{22}O_{11} + H_2O \qquad (10.4.1)$$

a molecule of water is lost. Recall that proteins are also formed from smaller amino acid molecules by condensation reactions involving the loss of water molecules. Disaccharides include sucrose (cane sugar used as a sweetener), lactose (milk sugar), and maltose (a product of the breakdown of starch).

Polysaccharides consist of many simple sugar units hooked together. One of the most important polysaccharides is **starch**, which is produced by plants for food storage. Animals produce a related material called **glycogen**. The chemical formula of starch is $(C_6H_{10}O_5)_n$, where n may represent a number as high as several hundreds. What this means is that the very large starch molecule consists of many units of $C_6H_{10}O_5$ joined together. For example, if n is 100, there are 6 times 100 carbon atoms, 10 times 100 hydrogen atoms, and 5 times 100 oxygen atoms in the molecule. The chemical formula of starch is $C_{600}H_{1000}O_{500}$.The atoms in a starch molecule are actually present as linked rings represented by the structure shown in Figure 10.4. Starch occurs in many foods, such as bread and cereals. It is readily digested by animals, including humans.

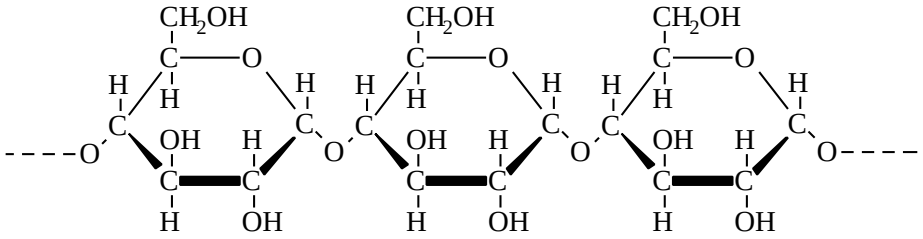


Figure 10.4 Part of a starch molecule showing units of $C_6H_{10}O_5$ condensed together.

Cellulose is a polysaccharide that is also made up of $C_6H_{10}O_5$ units. Molecules of cellulose are huge, with molecular masses of around 400,000. The cellulose

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structure (Figure 10.5) is similar to that of starch. Cellulose is produced by plants and forms the structural material of plant cell walls. Wood is about 60% cellulose, and cotton contains over 90% of this material. Fibers of cellulose are extracted from wood and pressed together to make paper.

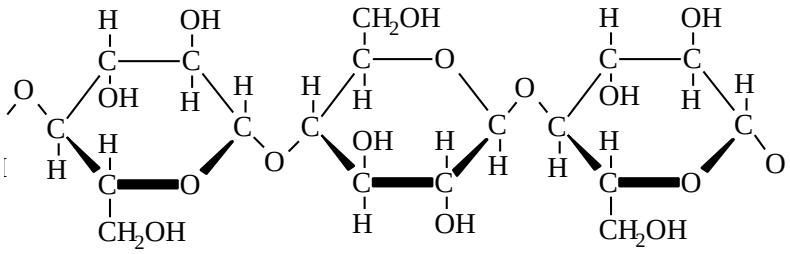


Figure 10.5 Part of the structure of cellulose.

Humans and most other animals cannot digest cellulose. Ruminant animals (cattle, sheep, goats, moose) have bacteria in their stomachs that break down cellulose into products that can be used by the animal. Chemical processes are available to convert cellulose to simple sugars by the reaction

$$\underset{\text{cellulose}}{(C_6H_{10}O_5)_n} + nH_2O \rightarrow \underset{\text{glucose}}{nC_6H_{12}O_6} \qquad (10.4.2)$$

where n may be 2000-3000. This involves breaking the linkages between units of $C_6H_{10}O_5$ by adding a molecule of H_2O at each linkage, a hydrolysis reaction. Large amounts of cellulose from wood, sugar cane, and agricultural products go to waste each year. The hydrolysis of cellulose enables these products to be converted to sugars, which can be fed to animals.

Carbohydrate groups are attached to protein molecules in a special class of materials called **glycoproteins**. Collagen is a crucial glycoprotein that provides structural integrity to body parts. It is a major constituent of skin, bones, tendons, and cartilage.

10.5 LIPIDS

Lipids are substances that can be extracted from plant or animal matter by organic solvents, such as chloroform, diethyl ether, or toluene (Figure 10.6). Whereas carbohydrates and proteins are characterized predominantly by the monomers (monosaccharides and amino acids) from which they are composed, lipids are defined essentially by their physical characteristic of organophilicity. The most common lipids are fats and oils composed of **triglycerides** formed from the alcohol glycerol, $CH_2(OH)CH(OH)CH_2(OH)$ and a long-chain fatty acid such as stearic acid, $CH_3(CH_2)_{16}C(O)OH$ (Figure 10.7). Numerous other biological materials, including waxes, cholesterol, and some vitamins and hormones, are classified as lipids. Common foods, such as butter and salad oils are lipids. The longer chain fatty acids, such as stearic acid, are also organic-soluble and are classified as lipids.

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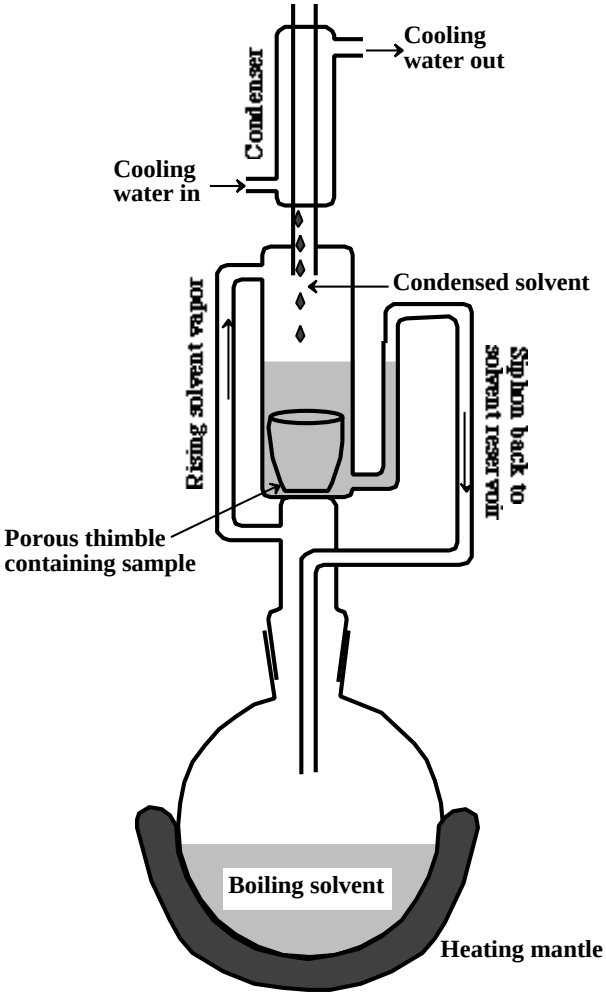


Figure 10.6 Lipids are extracted from some biological materials with a soxhelet extractor (above). The solvent is vaporized in the distillation flask by the heating mantle, rises through one of the exterior tubes to the condenser, and is cooled to form a liquid. The liquid drops onto the porous thimble containing the sample. Siphon action periodically drains the solvent back into the distillation flask. The extracted lipid collects as a solution in the solvent in the flask.

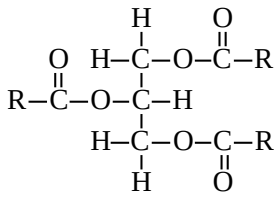


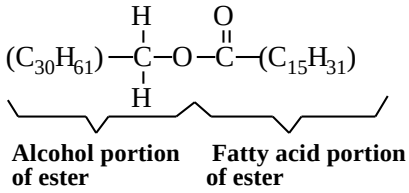
Figure 10.7 General formula of triglycerides, which make up fats and oils. The R group is from a fatty acid and is a hydrocarbon chain, such as $-(CH_2)_{16}CH_3$.

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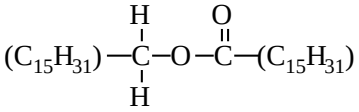
Lipids are toxicologically important for several reasons. Some toxic substances interfere with lipid metabolism, leading to detrimental accumulation of lipids. Many toxic organic compounds are poorly soluble in water, but are lipid-soluble, so that bodies of lipids in organisms serve to dissolve and store toxicants.

An important class of lipids consists of **phosphoglycerides** (glycerophosphatides), which may be regarded as triglyderides in which one of the acids bonded to glycerol is orthophosphoric acid. These lipids are especially important because they are essential constituents of cell membranes. These membranes consist of bilayers in which the hydrophilic phosphate ends of the molecules are on the outside of the membrane and the hydrophobic "tails" of the molecules are on the inside.

Waxes are also esters of fatty acids. However, the alcohol in a wax is not glycerol. The alcohol in waxes is often a very long-chain alcohol. For example, one of the main compounds in beeswax is myricyl palmitate,



in which the alcohol portion of the ester has a very large hydrocarbon chain. Waxes are produced by both plants and animals, largely as protective coatings. Waxes are found in a number of common products. Lanolin is one of these. It is the "grease" in sheep's wool. When mixed with oils and water, it forms stable colloidal emulsions consisting of extremely small oil droplets suspended in water. This makes lanolin useful for skin creams and pharmaceutical ointments. Carnauba wax occurs as a coating on the leaves of some Brazilian palm trees. Spermaceti wax is composed largely of cetyl palmitate


Cetyl palmitate

extracted from the blubber of the sperm whale. It is very useful in some cosmetics and pharmaceutical preparations.

Steroids are lipids found in living systems that all have the ring system shown in Figure 10.8 for cholesterol. Steroids occur in bile salts, which are produced by the liver and then secreted into the intestines. Their breakdown products give feces its characteristic color. Bile salts act upon fats in the intestine. They suspend very tiny fat droplets in the form of colloidal emulsions. This enables the fats to be broken down chemically and digested.

Some steroids are **hormones**. Hormones act as "messengers" from one part of the body to another. As such, they start and stop a number of body functions. Male and female sex hormones are examples of steroid hormones. Hormones are given off by glands in the body called **endocrine glands**. The locations of the important endocrine glands are shown in Figure 10.9.

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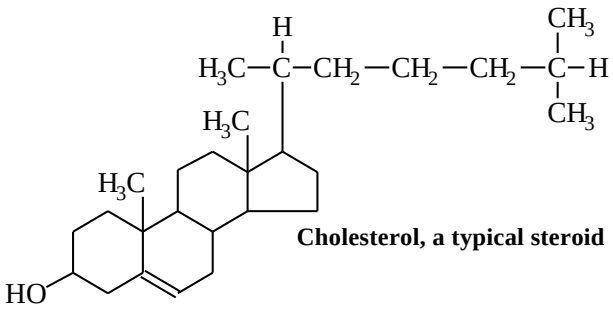


Figure 10.8 Steroids are characterized by the ring structure shown above for cholesterol.

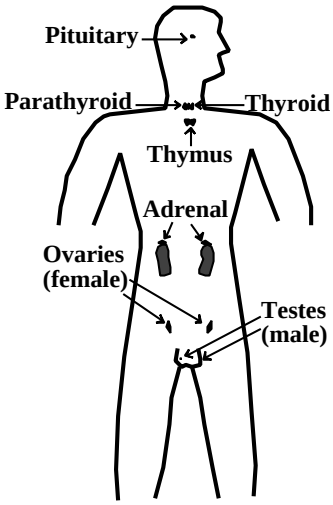


Figure 10.9 Locations of important endocrine glands.

10.6 ENZYMES

Catalysts are substances that speed up a chemical reaction without themselves being consumed in the reaction. The most sophisticated catalysts of all are those found in living systems. They bring about reactions that could not be performed at all, or only with great difficulty, outside a living organism. These catalysts are called **enzymes**. In addition to speeding up reactions by as much as ten to a hundred million-fold, enzymes are extremely selective in the reactions that they promote.

Enzymes are proteinaceous substances with highly specific structures that interact with particular substances or classes of substances called **substrates**. Enzymes act as catalysts to enable biochemical reactions to occur, after which they are regenerated intact to take part in additional reactions. The extremely high specificity with which enzymes interact with substrates results from their "lock and key" action based upon the unique shapes of enzymes as illustrated in Figure 10.10. This illustration shows that an enzyme "recognizes" a particular substrate by its molecular structure and binds to it to produce an **enzyme-substrate complex**. This com-

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plex then breaks apart to form one or more products different from the original enzyme, regenerating the unchanged enzyme, which is then available to catalyze additional reactions. The basic process for an enzyme reaction is, therefore,

$$\text{enzyme} + \text{substrate} \leftarrow\rightarrow \text{enzyme-substrate complex} \leftarrow\rightarrow \text{enzyme} + \text{product} \qquad (10.6.1)$$

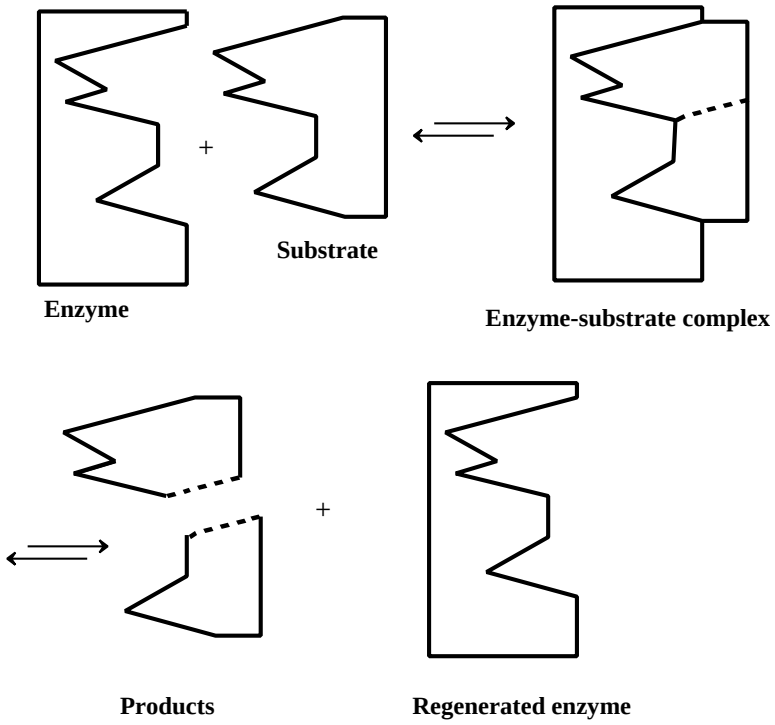


Figure 10.10 Representation of the "lock-and-key" mode of enzyme action that enables the very high specificity of enzyme-catalyzed reactions.

Several important things should be noted about this reaction. As shown in Figure 10.10, an enzyme acts on a specific substrate to form an enzyme-substrate complex because of the fit between their structures. As a result, something happens to the substrate molecule. For example, it might be split in two at a particular location. Then the enzyme-substrate complex comes apart, yielding the enzyme and products. The enzyme is not changed in the reaction and is now free to react again. Note that the arrows in the formula for enzyme reaction point both ways. This means that the reaction is **reversible**. An enzyme-substrate complex can simply go back to the enzyme and the substrate. The products of an enzymatic reaction can react with the enzyme to form the enzyme-substrate complex again. It, in turn, may again form the enzyme and the substrate. Therefore, the same enzyme may act to cause a reaction to go either way.

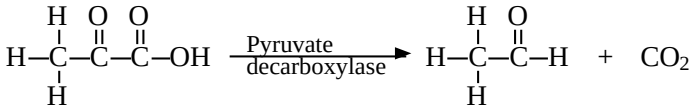
Some enzymes cannot function by themselves. In order to work, they must first be attached to **coenzymes**. Coenzymes normally are not protein materials. Some of the vitamins are important coenzymes.

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Enzymes are named for what they do. For example, the enzyme given off by the stomach, which splits proteins as part of the digestion process, is called *gastric proteinase*. The "gastric" part of the name refers to the enzyme's origin in the stomach. The "proteinase" denotes that it splits up protein molecules. The common name for this enzyme is pepsin. Similarly, the enzyme produced by the pancreas that breaks down fats (lipids) is called *pancreatic lipase*. Its common name is steapsin. In general, lipase enzymes cause lipid triglycerides to dissociate and form glycerol and fatty acids.

The enzymes mentioned above are **hydrolyzing enzymes**, which bring about the breakdown of high molecular weight biological compounds by the addition of water. This is one of the most important types of the reactions involved in digestion. The three main classes of energy-yielding foods that animals eat are carbohydrates, proteins, and fats. Recall that the higher carbohydrates humans eat are largely disaccharides (sucrose, or table sugar) and polysaccharides (starch). These are formed by the joining together of units of simple sugars, $C_6H_{12}O_6$, with the elimination of an H_2O molecule at the linkage where they join. Proteins are formed by the condensation of amino acids, again with the elimination of a water molecule at each linkage. Fats are esters that are produced when glycerol and fatty acids link together. A water molecule is lost for each of these linkages when a protein, fat, or carbohydrate are synthesized. In order for these substances to be used as a food source, the reverse process must occur to break down large, complicated molecules of protein, fat, or carbohydrate to simple, soluble substances that can penetrate a cell membrane and take part in chemical processes in the cell. This reverse process is accomplished by hydrolyzing enzymes.

Biological compounds with long chains of carbon atoms are broken down into molecules with shorter chains by the breaking of carbon-carbon bonds. This commonly occurs by the elimination of $-CO_2H$ groups from carboxylic acids. For example, *pyruvic decarboxylase* enzyme acts upon pyruvic acid,



Pyruvic acid **Acetaldehyde** (10.6.2)

to split off CO_2 and produce a compound with one less carbon. It is by such carbon-by-carbon breakdown reactions that long chain compounds are eventually degraded to CO_2 in the body, or that long-chain hydrocarbons undergo biodegradation by the action of bacteria.

Oxidation and reduction are the major reactions for the exchange of energy in living systems. Cellular respiration, mentioned in Section 10.2, is an oxidation reaction in which a carbohydrate, $C_6H_{12}O_6$, is broken down to carbon dioxide and water with the release of energy.

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy} \quad (10.6.3)$$

Actually, such an overall reaction occurs in living systems by a complicated series of individual steps. Some of these steps involve oxidation. The enzymes that bring

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about oxidation in the presence of free O_2 are called **oxidases**. In general, biological oxidation-reduction reactions are catalyzed by **oxidoreductase enzymes**.

In addition to the types of enzymes discussed above, there are many enzymes that perform miscellaneous duties in living systems. Typical of these are **isomerases**, which form isomers of particular compounds. For example, there are several simple sugars with the formula $C_6H_{12}O_6$. However, only glucose can be used directly for cell processes. The other isomers are converted to glucose by the action of isomerases. **Transferase enzymes** move chemical groups from one molecule to another, **lyase enzymes** remove chemical groups without hydrolysis and participate in the formation of C=C bonds or addition of species to such bonds, and **ligase enzyme**s work in conjunction with ATP (adenosine triphosphate, a high-energy molecule that plays a crucial role in energy-yielding, glucose-oxidizing metabolic processes) to link molecules together with the formation of bonds such as carbon-carbon or carbon-sulfur bonds.

Enzyme action may be affected by many different things. Enzymes require a certain hydrogen ion concentration to function best. For example, gastric proteinase requires the acid environment of the stomach to work well. When it passes into the much less acidic intestines, it stops working. This prevents damage to the intestine walls, which would occur if the enzyme tried to digest them. Temperature is critical. Not surprisingly, the enzymes in the human body work best at around 98.6°F (37°C), which is the normal body temperature. Heating these enzymes to around 140°F permanently destroys them. Some bacteria that thrive in hot springs have enzymes that work best at relatively high temperatures. Other "cold-seeking" bacteria have enzymes adapted to near the freezing point of water.

One of the greatest concerns regarding the effects of surroundings upon enzymes is the influence of toxic substances. A major mechanism of toxicity is the alteration or destruction of enzymes by agents such as cyanide, heavy metals, or organic compounds, such as insecticidal parathion. An enzyme that has been destroyed obviously cannot perform its designated function, whereas one that has been altered may either not function at all or may act improperly. Toxicants can affect enzymes in several ways. Parathion, for example, bonds covalently to the nerve enzyme acetylcholinesterase, which can then no longer serve to stop nerve impulses. Heavy metals tend to bind to sulfur atoms in enzymes (such as sulfur from the amino acid cysteine shown in Figure 10.2), thereby altering the shape and function of the enzyme. Enzymes are denatured by some poisons, causing them to "unravel" so that the enzyme no longer has its crucial specific shape.

10.7 NUCLEIC ACIDS

The "essence of life" is contained in **deoxyribonucleic acid** (**DNA**, which stays in the cell nucleus) and **ribonucleic acid** (**RNA**, which functions in the cell cytoplasm). These substances, which are known collectively as **nucleic acids**, store and pass on essential genetic information that controls reproduction and protein synthesis.

The structural formulas of the monomeric constituents of nucleic acids are given in Figure 10.11. These are pyrimidine or purine nitrogen-containing bases, two sugars, and phosphate. DNA molecules are made up of the nitrogen-containing bases

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adenine, guanine, cytosine, and thymine; phosphoric acid (H_3PO_4); and the simple sugar 2-deoxy-β-D-ribofuranose (commonly called deoxyribose). RNA molecules are composed of the nitrogen-containing bases adenine, guanine, cytosine, and uracil; phosphoric acid (H_3PO_4); and the simple sugar β-D-ribofuranose (ribose).

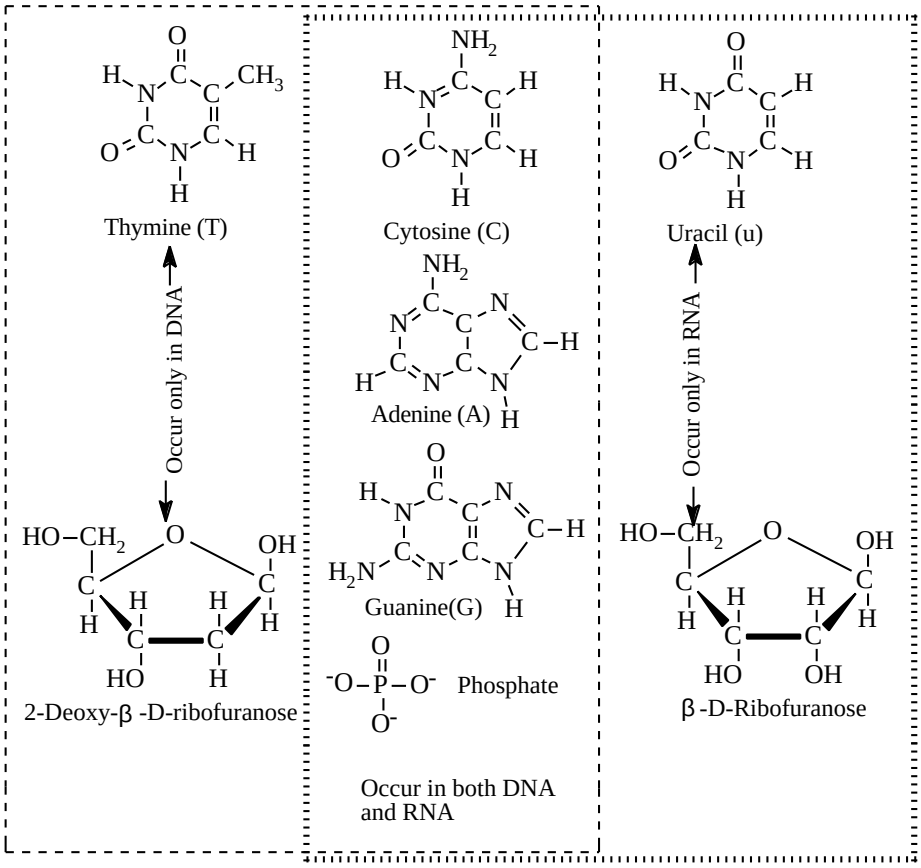
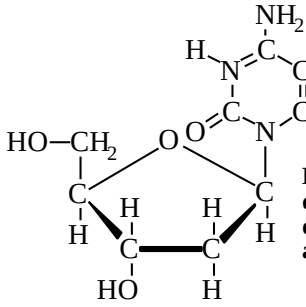


Figure 10.11 Constituents of DNA (enclosed by ----) and of RNA (enclosed by ⋯⋯).

The formation of nucleic acid polymers from their monomeric constituents can be viewed as the following steps.

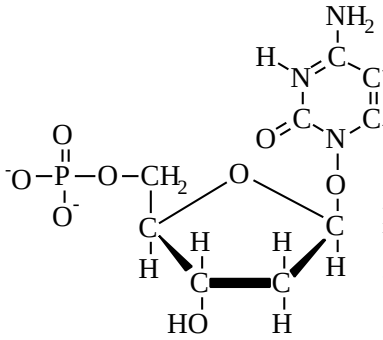
- Monosaccharide (simple sugar) + cyclic nitrogenous base yields **nucleoside**:



Deoxyctidine formed by the dimerization of cytosine and deoxyribose with the elimination of a molecule of H_2O.

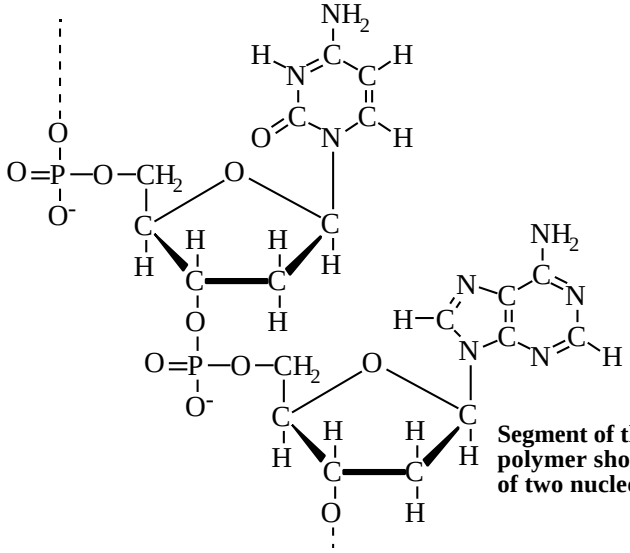
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- Nucleoside + phosphate yields **phosphate ester nucleotide**.



Nucleotide formed by the bonding of a phosphate group to deoxyctidine

- Polymerized nucleotide yields **nucleic acid**, as shown by the structure below. In the nucleic acid, the phosphate negative charges are neutralized by metal cations (such as Mg^{2+}) or positively charged proteins (histones).



Segment of the DNA polymer showing linkage of two nucleotides

Molecules of DNA are huge with molecular weights greater than one billion. Molecules of RNA are also quite large. The structure of DNA is that of the famed "double helix." It was figured out in 1953 by an American scientist, James D. Watson, and Francis Crick, a British scientist. They received the Nobel prize for this scientific milestone in 1962. This model visualizes DNA as a so-called double α-helix structure of oppositely wound polymeric strands held together by hydrogen bonds between opposing pyrimidine and purine groups. As a result, DNA has both a primary and a secondary structure; the former is due to the sequence of nucleotides in the individual strands of DNA and the latter results from the α-helix interaction of the two strands. In the secondary structure of DNA, only cytosine can be opposite guanine and only thymine can be opposite adenine and vice versa. Basically, the structure of DNA is that of two spiral ribbons "counter-wound" around each other as

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illustrated in Figure 10.12. The two strands of DNA are **complementary**. This means that a particular portion of one strand fits like a key in a lock with the corresponding portion of another strand. If the two strands are pulled apart, each manufactures a new complementary strand, so that two copies of the original double helix result. This occurs during cell reproduction.

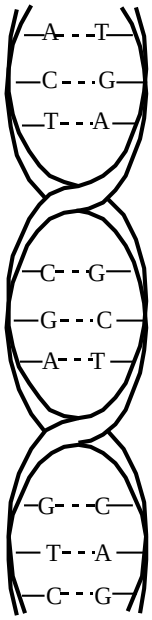


Figure 10.12 Representation of the double helix structure of DNA showing the allowed base pairs held together by hydrogen bonding between the phosphate/sugar polymer "backbones" of the two strands of DNA. The letters stand for adenine (A), cytosine (C), guanine (G), and thymine (T). The dashed lines, ---, represent hydrogen bonds.

The molecule of DNA is sort of like a coded message. This "message," the genetic information contained in and transmitted by nucleic acids, depends upon the sequence of bases from which they are composed. It is somewhat like the message sent by telegraph, which consists only of dots, dashes, and spaces in between. The key aspect of DNA structure that enables storage and replication of this information is the double helix structure of DNA mentioned above.

Portions of the DNA double helix may unravel, and one of the strands of DNA may produce a strand of RNA. This substance then goes from the cell nucleus out into the cell and regulates the synthesis of new protein. In this way, DNA regulates the function of the cell and acts to control life processes.

Nucleic Acids in Protein Synthesis

Whenever a new cell is formed, the DNA in its nucleus must be accurately reproduced from the parent cell. Life processes are absolutely dependent upon accurate protein synthesis as regulated by cell DNA. The DNA in a single cell must be capable of directing the synthesis of up to 3000 or even more different proteins. The directions for the synthesis of a single protein are contained in a segment of

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DNA called a **gene**. The process of transmitting information from DNA to a newly synthesized protein involves the following steps:

- The DNA undergoes **replication**. This process involves separation of a segment of the double helix into separate single strands that then replicate such that guanine is opposite cytosine (and vice versa) and adenine is opposite thymine (and vice versa). This process continues until a complete copy of the DNA molecule has been produced.
- The newly replicated DNA produces **messenger RNA** (**m-RNA**), a complement of the single strand of DNA, by a process called **transcription**.
- A new protein is synthesized using m-RNA as a template to determine the order of amino acids in a process called **translation**.

Modified DNA

DNA molecules may be modified by the unintentional addition or deletion of nucleotides or by substituting one nucleotide for another. The result is a **mutation** that is transmittable to offspring. Mutations can be induced by chemical substances. This is a major concern from a toxicological viewpoint because of the detrimental effects of many mutations and because substances that cause mutations often cause cancer as well. DNA malfunction may result in birth defects, and the failure to control cell reproduction results in cancer. Radiation from X-rays and radioactivity also disrupts DNA and may cause mutation.

10.8 RECOMBINANT DNA AND GENETIC ENGINEERING

As noted above, segments of DNA contain information for the specific syntheses of particular proteins. Within the last two decades it has become possible to transfer this information between organisms by means of **recombinant DNA technology**, which has resulted in a new industry based on **genetic engineering**. Most often, the recipient organisms are bacteria, which can be reproduced (cloned) over many orders of magnitude from a cell that has acquired the desired qualities. Therefore, to synthesize a particular substance, such as human insulin or growth hormone, the required genetic information can be transferred from a human source to bacterial cells, which then produce the substance as part of their metabolic processes.

The first step in recombinant DNA gene manipulation is to lyze (“open up”) a donor cell to remove needed DNA material by using enzyme action to cut the sought-after genes from the donor DNA chain. These are next spliced into small DNA molecules. These molecules, called **cloning vehicles**, are capable of penetrating the host cell and becoming incorporated into its genetic material. The modified host cell is then reproduced many times and carries out the desired biosynthesis.

Early concerns about the potential of genetic engineering to produce “monster organisms” or new and horrible diseases have been largely allayed, although caution is still required with this technology. In the environmental area, genetic engineering offers some hope for the production of bacteria engineered to safely destroy troublesome wastes and to produce biological substitutes for environmentally damaging synthetic pesticides.

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Arguably the greatest uses of recombinant DNA so far has been in the production of so-called transgenic crops with special genetic properties that enable them to be particularly productive. Corn and potatoes have been developed that produce an insecticide normally made by bacteria. Soybeans have been genetically engineered to be resistant to commercial herbicides. Cotton and squash are other plants with genetically engineered properties that increase yields.

10.9 METABOLIC PROCESSES

Biochemical processes that involve the alteration of biomolecules fall under the category of **metabolism**. Metabolic processes can be divided into the two major categories of **anabolism** (synthesis) and **catabolism** (degradation of substances). An organism can use metabolic processes to yield energy or to modify the constituents of biomolecules.

Energy-Yielding Processes

Organisms can gain energy by the following three processes:

- **Respiration** in which organic compounds undergo catabolism that requires molecular oxygen (**aerobic respiration**) or that occurs in the absence of molecular oxygen (**anaerobic repiration**). Aerobic respiration uses the **Krebs cycle** to obtain energy from the following reaction:

 $C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O + \text{energy}$

 About half of the energy released is converted to short-term stored chemical energy, particularly through the synthesis of **adenosine triphosphate** (**ATP**) nucleoside. For longer-term energy storage, glycogen or starch polysaccharides are synthesized, and for still longer-term energy storage, lipids (fats) are generated and retained by the organism.

- **Fermentation**, which differs from respiration in not having an electron transport chain. Yeasts produce ethanol from sugars by fermentation:

 $C_6H_{12}O_6 \rightarrow 2CO_2 + 2C_2H_5OH$

- **Photosynthesis** in which light energy captured by plant and algal chloroplasts is used to synthesize sugars from carbon dioxide and water:

 $6CO_2 + 6H_2O + h\nu \rightarrow C_6H_{12}O_6 + 6O_2$

Plants cannot always get the energy that they need from sunlight. During the dark they must use stored food. Plant cells, like animal cells, contain mitochondria in which stored food is converted to energy by cellular respiration.

Plant cells, which use sunlight for energy and CO_2 for carbon, are said to be **autotrophic**. In contrast, animal cells must depend upon organic material manufactured by plants for their food. These are called **heterotrophic** cells. They act as “middlemen” in the chemical reaction between oxygen and food material using the energy from the reaction to carry out their life processes.

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CHAPTER SUMMARY

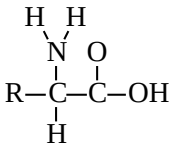
The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

The biomolecules that constitute matter in living organisms are often high-molecular-mass [1]_____ divided into the categories of [2]_____ _____. In respect to affinity for water versus lipids, the behavior of a substance in a biological system depends to a large extent upon whether the substance is [3]_____ or [4]_____. The two major kinds of cells are [5]_____ _____ cells that have a defined nucleus and [6]_____ cells that do not. Several major features of the eukaryotic cell are [7]_____ _____ _____. Three other features characteristic of plant cells are [8]_____ _____. Proteins are macromolecular biomolecules composed of [9]_____. A generalized structure for amino acids is [10]_____, where "R" represents groups characteristic of each amino acid. Amino acids are bonded together in proteins by a specific arrangement of atoms and bonds called a [11]_____. Casein is a protein that functions as a [12]_____, hemoglobin is a [13]_____ _____ protein, and collagen is a [14]_____ protein. Proteins exhibit [15]_____ different orders of structure, the first of which is determined by the [16]_____. Protein denaturation consists of disruption of [17]_____ _____. Carbohydrates have the approximate simple formula [18]_____. The molecular formula of glucose is [19]_____. Polysaccharides are carbohydrates that consist of many [20]_____. An important polysaccharide produced by plants for food storage is [21]_____. Cellulose is a polysaccharide produced by [22]_____ that forms [23]_____. Substances that can be extracted from plant or animal matter by organic solvents, such as chloroform are called [24]_____. The most common lipids are triglycerides formed from [25]_____ _____. Two reasons that lipids are toxicologically important are that [26]_____ _____ _____. A special class of lipids with a characteristic ring system, such as that in cholesterol, consists of [27] _____. Some steroids are [28]_____ that act as "messengers" from one part of the body to another. Enzymes are proteinaceous substances with highly specific structures that function as biochemical [29]_____ and interact with particular substances or classes of substances called [30]_____. Enzymes are very specific in the kinds of substance that they interact with because of their unique [31]_____. In

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order to work, some enzymes must first be attached to [32]_____. Enzymes are named for [33]_____. For example, *gastric proteinase* comes from the [34]_____ and acts to [35]_____ _____. It is an example of a general class of enzymes called [36]_____. As another example, biological oxidation-reduction reactions are catalyzed by [37]_____ _____. Deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) are the two major kinds of [38]_____. The monomers from which they are composed are [39]_____ _____. Cell DNA regulates synthesis of [40]_____. Biochemical processes that involve the alteration of biomolecules are termed [41]_____ _____. The three processes by which organisms utilize energy are [42]_____ _____.

Answers to Chapter Summary

1. polymers
2. carbohydrates, proteins, lipids, and nucleic acids
3. hydrophilic
4. hydrophobic
5. eukaryotic
6. prokaryotic
7. cell membrane, cell nucleus, cytoplasm, mitochondria, ribosomes, endoplasmic reticulum, lysosome, golgi bodies
8. cell walls, vacuoles, and chloroplasts
9. amino acids
10. 
11. peptide linkage
12. nutrient
13. transport
14. structural
15. four
16. order of amino acids
17. secondary, tertiary, and quaternary protein structures
18. CH_2O
19. $C_6H_{12}O_6$
20. simple sugar units hooked together
21. starch
22. plants
23. the structural material of plant cell walls
24. lipids
25. glycerol and long-chain fatty acids

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26. some toxic substances interfere with lipid metabolism, and many toxic organic compounds are lipid-soluble
27. steroids
28. hormones
29. catalysts
30. substrates
31. shapes or structures
32. coenzymes
33. what they do
34. stomach
35. split apart protein molecules
36. hydrolyzing enzymes
37. oxidoreductase enzymes
38. nucleic acids
39. nitrogen-containing bases, phosphoric acid, and simple sugars
40. proteins
41. metabolism
42. respiration, fermentation, and photosynthesis

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QUESTIONS AND PROBLEMS

1. What is the toxicological importance of lipids? How do lipids relate to hydrophobic ("water-disliking") pollutants and toxicants?
2. What is the function of a hydrolase enzyme?
3. Match the cell structure on the left with its function on the right, below:

A. Mitochondria	1. Toxicant metabolism
B. Endoplasmic reticulum	2. Fills the cell
C. Cell membrane	3. Deoxyribonucleic acid
D. Cytoplasm	4. Mediate energy conversion and utilization
E. Cell nucleus	5. Encloses the cell and regulates the passage of materials into and out of the cell interior

4. The formula of simple sugars is $C_6H_{12}O_6$. The simple formula of higher carbohydrates is $C_6H_{10}O_5$. Of course, many of these units are required to make a molecule of starch or cellulose. If higher carbohydrates are formed by joining together molecules of simple sugars, why is there a difference in the ratios of C, H, and O atoms in the higher carbohydrates as compared with the simple sugars?
5. Why does wood contain so much cellulose?
6. What would be the chemical formula of a *tri*saccharide made by the bonding together of three simple sugar molecules?
7. The general formula of cellulose can be represented as $(C_6H_{10}O_5)_x$. If the molecular weight of a molecule of cellulose is 400,000, what is the estimated value of x?
8. During one month, a factory for the production of simple sugars, $C_6H_{12}O_6$, by the hydrolysis of cellulose processes one million kilograms of cellulose. The percentage of cellulose that undergoes the hydrolysis reaction is 40%. How many kg of water are consumed in the hydrolysis of cellulose each month?

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9. What is the structure of the largest group of atoms common to all amino acid molecules?

10. Glycine and phenylalanine can join together to form two different dipeptides. What are the structures of these two dipeptides?

11. One of the ways in which two parallel protein chains are joined together, or crosslinked, is by way of an —S—S— link. What amino acid do you think might be most likely to be involved in such a link? Explain your choice.

12. Fungi, which break down wood, straw, and other plant material, have what are called "exoenzymes." Fungi have no teeth and cannot break up plant material physically by force. Knowing this, what do you suppose an exoenzyme is? Explain how you think it might operate in the process by which fungi break down something as tough as wood.

13. Many fatty acids of lower molecular weight have a bad odor. Speculate as to the reasons that rancid butter has a bad odor. What chemical compound is produced that has a bad odor? What sort of chemical reaction is involved in its production?

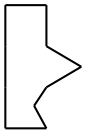
14. The long-chain alcohol with 10 carbons is called decanol. What do you think would be the formula of decyl stearate? To what class of compounds would it belong?

15. Write an equation for the chemical reaction between sodium hydroxide and cetyl stearate. What are the products?

16. What are two endocrine glands that are found only in females? Which of these glands is found only in males?

17. The action of bile salts is a little like that of soap. What function do bile salts perform in the intestine? Look up the action of soaps, and explain how you think bile salts may function somewhat like soap.

18. If the structure of an enzyme is illustrated as,



how should the structure of its substrate be represented?

19. Look up the structures of ribose and deoxyribose. Explain where the "deoxy" came from in the name deoxyribose.

20. In what respect is an enzyme and its substrate like two opposite strands of DNA?

21. For what discovery are Watson and Crick noted?

22. Why does an enzyme no longer work if it is denatured?

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Manahan, Stanley E. "ENVIRONMENTAL CHEMISTRY OF WATER"
Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

11 ENVIRONMENTAL CHEMISTRY OF WATER

11.1 INTRODUCTION

This is the first of the remaining chapters in this book that deal with environmental chemistry. In the discussion of this topic, the environment will be viewed as consisting of five spheres—the hydrosphere, atmosphere, geosphere, biosphere, and anthrosphere. Although often not acknowledged as one of the environmental spheres, the anthrosphere, consisting of the things humans construct, use, and do in the environment, is very important to consider as one of these five spheres. By so doing, we can begin the essential process of using our human activities to preserve and enhance the Earth environment upon which we and all living organisms depend.

Water composes one of the five "spheres" in which environmental chemistry is discussed. This chapter introduces the environmental chemistry of water. Chapter 12 covers water pollution, and Chapter 13 discusses water treatment.

11.2 THE PROPERTIES OF WATER, A UNIQUE SUBSTANCE

Water has a number of unique properties that are essential to life and that determine its environmental chemical behavior. Many of these properties are due to water's polar molecular structure and its ability to form hydrogen bonds (discussed in Chapter 3, Sections 7.3 and 7.4). The more important special characteristics of water are summarized in Table 11.1.

11.3 SOURCES AND USES OF WATER: THE HYDROLOGIC CYCLE

The world's water supply is found in the five parts of the **hydrologic cycle** (Figure 11.1). About 97% of Earth's water is found in the oceans. Another fraction is present as water vapor in the atmosphere (clouds). Some water is contained in the solid state as ice and snow in snowpacks, glaciers, and the polar ice caps. Surface

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Table 11.1 Important Properties of Water

Property	Effects and Significance
Excellent solvent	Transport of nutrients and waste products, making biological processes possible in an aqueous medium
Highest dielectric constant of any common liquid	High solubility of ionic substances and their ionization in solution
Higher surface tension than any other liquid	Controlling factor in physiology; governs drop and surface phenomena
Transparent to visible and longer-wavelength fraction of ultraviolet light	Colorless, allowing light required for photosynthesis to reach considerable depths in bodies of water
Maximum density as a liquid at 4°C	Ice floats; vertical circulation restricted in stratified bodies of water
Higher heat of evaporation than any other material	Determines transfer of heat and water molecules between the atmosphere and bodies of water
Higher latent heat of fusion than any other liquid except ammonia	Temperature stabilized at the freezing point of water
Higher heat capacity than any other liquid except ammonia	Stabilization of temperatures of organisms and geographical regions

water is found in lakes, streams, and reservoirs. Groundwater is located in aquifers underground.

There is a strong connection between the *hydrosphere*, where water is found, and the *lithosphere*, or land; human activities affect both. For example, disturbance of land by conversion of grasslands or forests to agricultural land or intensification of agricultural production may reduce vegetation cover, decreasing **transpiration** (loss of water vapor by plants) and affecting the microclimate. The result is increased rain runoff, erosion, and accumulation of silt in bodies of water. The nutrient cycles may be accelerated, leading to nutrient enrichment of surface waters. This, in turn, can profoundly affect the chemical and biological characteristics of bodies of water.

The water that humans use is primarily fresh surface water and groundwater, the sources of which may differ from each other significantly. In arid regions, a small fraction of the water supply comes from the ocean, a source that is likely to become more important as the world's supply of fresh water dwindles relative to demand. Saline or brackish groundwaters may also be utilized in some areas.

In the continental United States, an average of approximately 1.48×10^{13} liters of water fall as precipitation each day, which translates to 76 cm per year. Of that

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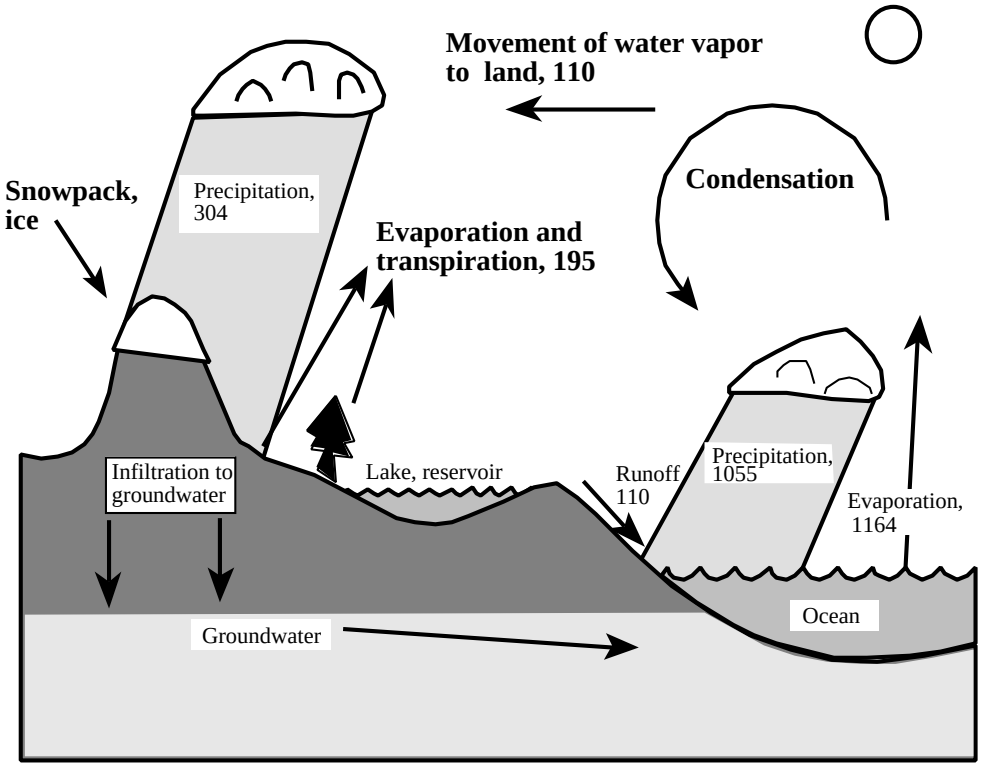


Figure 11.1 The hydrologic cycle, quantities of water in trillions of liters per day.

amount, approximately 1.02×10^{13} liters per day, or 53 cm per year, are lost by evaporation and transpiration. Thus, the water theoretically available for use is approximately 4.6×10^{12} liters per day, or only 23 centimeters per year. At present, the U.S. uses 1.6×10^{12} liters per day, or 8 centimeters of the average annual precipitation, an almost tenfold increase from a usage of 1.66×10^{11} liters per day at the turn of the century. Even more striking is the per capita increase from about 40 liters per day in 1900 to around 600 liters per day now. Much of this increase is accounted for by high agricultural and industrial use, which each account for approximately 46% of total consumption. Municipal use consumes the remaining 8%.

Since about 1980, however, water use in the U.S. has shown an encouraging trend with total consumption down by about 9% during a time in which population grew 16%, according to figures compiled by the U.S. Geological Survey.[1] This trend, which is illustrated in Figure 11.2, has been attributed to the success of efforts to conserve water, especially in the industrial (including power generation) and agricultural sectors. Conservation and recycling have accounted for much of the decreased use in the industrial sector. Irrigation water has been used much more efficiently by replacing spray irrigators, which lose large quantities of water to the action of wind and to evaporation, with irrigation systems that apply water directly to soil. Trickle irrigation systems that apply just the amount of water needed directly to plant roots are especially efficient.

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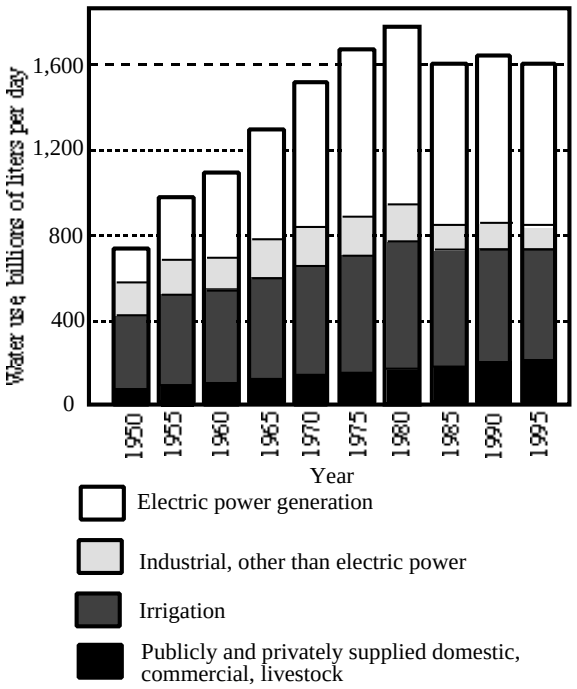


Figure 11.2 Trends in water use in the United States (data from U.S. Geological Survey).

A major problem with water supply is its nonuniform distribution with location and time. As shown in Figure 11.3, precipitation falls unevenly in the continental U.S. This causes difficulties because people in areas with low precipitation often consume more water than people in regions with more rainfall. Rapid population growth in the more arid southwestern states of the U.S. during the last four decades has further aggravated the problem. Water shortages are becoming more acute in this region which contains six of the nation's 11 largest cities (Los Angeles, Houston, Dallas, San Diego, Phoenix, and San Antonio). Other problem areas include the Northeast, plagued by deteriorating water systems; Florida, where overdevelopment of coastal areas threatens Lake Okeechobee; and the High Plains, ranging from the Texas panhandle to Nebraska, where irrigation demands on the Ogalalla aquifer are dropping the water table steadily with no hope of recharge. These problems are minor, however, in comparison with those in some parts of Africa, where water shortages are contributing to real famine conditions.

11.4 THE CHARACTERISTICS OF BODIES OF WATER

The physical condition of a body of water strongly influences the chemical and biological processes that occur in water. **Surface water** is found primarily in streams, lakes, and reservoirs. **Wetlands** are productive flooded areas in which the water is shallow enough to enable growth of bottom-rooted plants. **Estuaries** constitute another type of body of water, consisting of arms of the ocean into which streams flow. The mixing of fresh and salt water gives estuaries unique chemical and

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biological properties. Estuaries are the breeding grounds of much marine life, which makes their preservation very important.

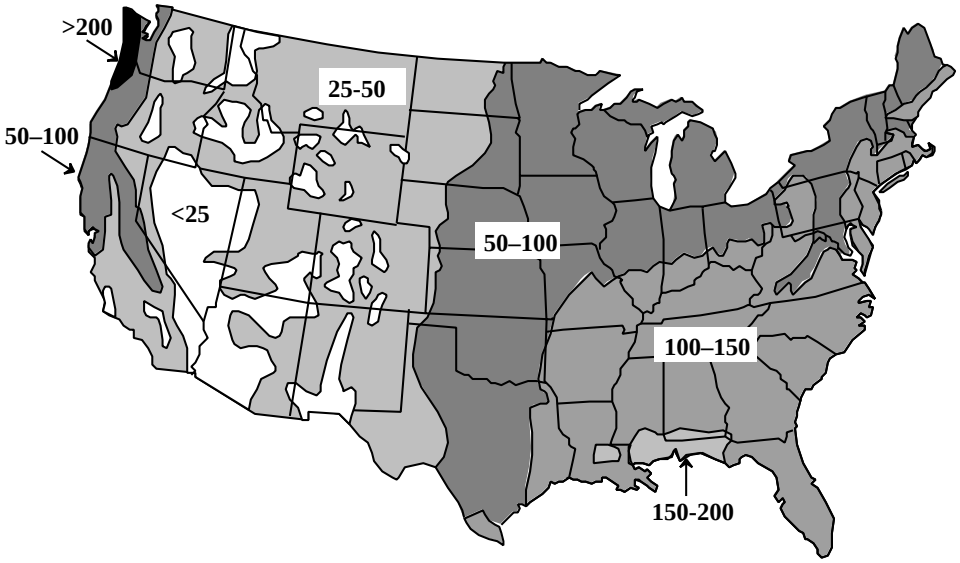


Figure 11.3 Distribution of precipitation in the continental U.S., showing average annual rainfall in centimeters.

Water's unique temperature-density relationship results in the formation of distinct layers within nonflowing bodies of water, as shown in Figure 11.4. During the summer a surface layer (**epilimnion**) is heated by solar radiation and, because of its lower density, floats upon the bottom layer, or **hypolimnion**. This phenomenon is called **thermal stratification.** When an appreciable temperature difference exists between the two layers, they do not mix, but behave independently and have very dif-

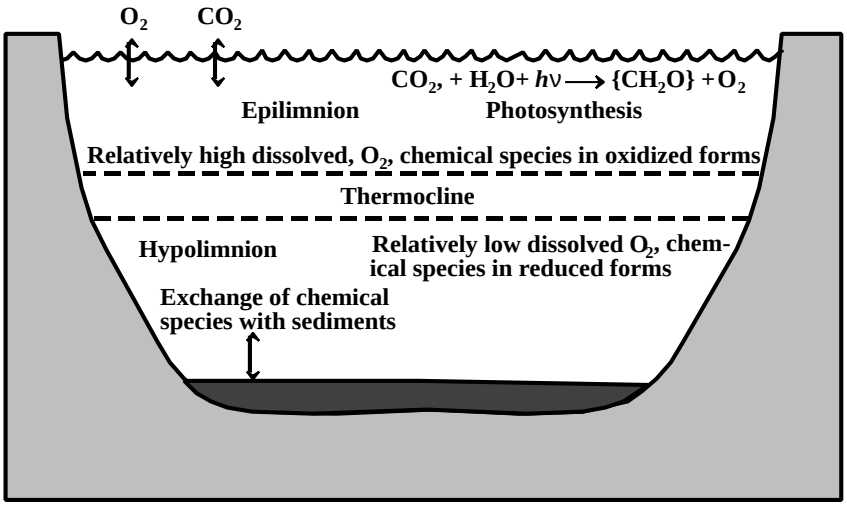


Figure 11.4 Stratification of a lake.

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ferent chemical and biological properties. The epilimnion, which is exposed to light, may have a heavy growth of algae. As a result of exposure to the atmosphere and (during daylight hours) because of the photosynthetic activity of algae, the epilimnion contains relatively higher levels of dissolved oxygen and generally is aerobic. Because of the presence of O_2, oxidized species predominate in the epilimnion. In the hypolimnion, consumption of O_2 by bacterial action on biodegradable organic material may cause the water to become anaerobic. As a consequence, chemical species in a relatively reduced form tend to predominate in the hypolimnion.

The chemistry and biology of the Earth's vast oceans are unique because of the ocean's high salt content, great depth, and other factors. Oceanographic chemistry is a discipline in its own right. The environmental problems of the oceans have increased greatly in recent years because of ocean dumping of pollutants, oil spills, and increased utilization of natural resources from the oceans.

11.5 AQUATIC CHEMISTRY

Figure 11.5 summarizes important aspects of **aquatic chemistry** applied to environmental chemistry. As shown in this figure, a number of chemical phenomena occur in water. Many aquatic chemical processes are influenced by the action of algae and bacteria in water. For example, Figure 11.5 shows that algal photosynthesis fixes inorganic carbon from HCO_3^- ion in the form of biomass (represented as $\{CH_2O\}$), in a process that also produces carbonate ion, CO_3^{2-}. Carbonate undergoes an acid-base reaction to produce OH^- ion and raise the pH, or it reacts with Ca^{2+} ion to precipitate solid $CaCO_3$. Most of the many oxidation-reduction reactions that occur in water are mediated (catalyzed) by bacteria. For example, bacteria convert inorganic nitrogen largely to ammonium ion, NH_4^+, in the oxygen-deficient (anaer-

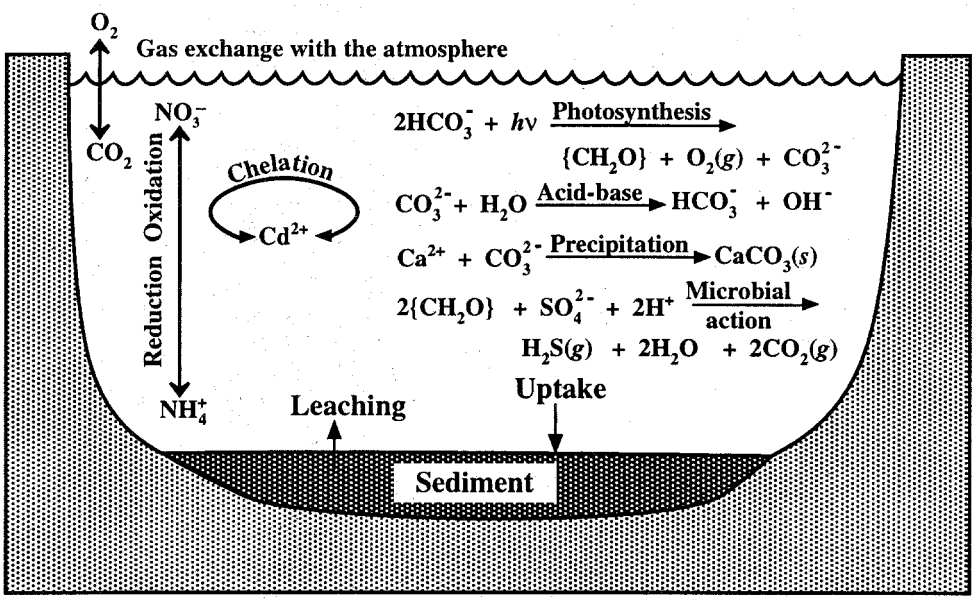


Figure 11.5 Major aquatic chemical processes.

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obic) lower layers of a body of water. Near the surface, where O_2 is available, bacteria convert inorganic nitrogen to nitrate ion, NO_3^-. Metals in water may be bound to organic chelating agents, such as pollutant nitrilotriacetic acid (NTA) or naturally occurring fulvic acids. Gases are exchanged with the atmosphere, and various solutes are exchanged between water and sediments in bodies of water.

Several important characteristics of unpolluted water should be noted. One of these is **gas solubility**. Since it is required to support aquatic life and maintain water quality, oxygen is the most important dissolved gas in water. Water in equilibrium with air at 25°C contains 8.3 milligrams per liter (mg/L) of dissolved O_2. Water **alkalinity** (see Section 11.6) is defined as the ability of solutes in water to neutralize added strong acid. Water **hardness** is due to the presence of calcium ion, Ca^{2+}, and, to a lesser extent, magnesium ion, Mg^{2+}.

11.6 ALKALINITY AND ACIDITY

Alkalinity

The capacity of water to accept H^+ ions (protons) is called **alkalinity**. Alkalinity is important in water treatment and in the chemistry and biology of natural waters. Frequently, the alkalinity of water must be known to calculate the quantities of chemicals to be added in treating the water. Highly alkaline water often has a high pH and generally contains elevated levels of dissolved solids. These characteristics may be detrimental for water to be used in boilers, food processing, and municipal water systems. Alkalinity serves as a pH buffer and reservoir for inorganic carbon, thus helping to determine the ability of water to support algal growth and other aquatic life. It is used by biologists as a measure of water fertility. Generally, the basic species responsible for alkalinity in water are bicarbonate ion, carbonate ion, and hydroxide ion:

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \quad (11.6.1)$$

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \quad (11.6.2)$$

$$OH^- + H^+ \rightarrow H_2O \quad (11.6.3)$$

Other, usually minor, contributors to alkalinity are ammonia and the conjugate bases of phosphoric, silicic, boric, and organic acids.

It is important to distinguish between high *basicity*, manifested by an elevated pH, and high *alkalinity*, the capacity to accept H^+. Whereas pH is an *intensity* factor, alkalinity is a *capacity* factor. This can be illustrated by comparing a solution of 1.00×10^{-3} M NaOH with a solution of 0.100 M $NaHCO_3$. The sodium hydroxide solution is quite basic, with a pH of 11, but a liter of this solution will neutralize only 1.00×10^{-3} mole of acid. The pH of the sodium bicarbonate solution is 8.34, much lower than that of the NaOH. However, a liter of the sodium bicarbonate solution will neutralize 0.100 mole of acid; therefore, its alkalinity is 100 times that of the more basic NaOH solution.

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As an example of a water-treatment process in which water alkalinity is important, consider the use of *filter alum*, $Al_2(SO_4)_3 \cdot 18H_2O$ as a coagulant. The hydrated aluminum ion is acidic, and, when it is added to water, it reacts with base to form gelatinous aluminum hydroxide,

$$Al(H_2O)_6^{3+} + 3OH^- \rightarrow Al(OH)_3(s) + 6H_2O \quad (11.6.4)$$

which settles and carries suspended matter with it. This reaction removes alkalinity from the water. Sometimes, the addition of more alkalinity is required to prevent the water from becoming too acidic.

In engineering terms, alkalinity frequently is expressed in units of mg/L of $CaCO_3$, based upon the following acid-neutralizing reaction:

$$CaCO_3 + 2H^+ \rightarrow Ca^{2+} + CO_2 + H_2O \quad (11.6.5)$$

The equivalent weight of calcium carbonate is one-half its formula weight because only one-half of a $CaCO_3$ molecule is required to neutralize one OH^-. Expressing alkalinity in terms of mg/L of $CaCO_3$ can, however, lead to confusion, and equivalents/L is preferable notation for the chemist.

Acidity

Acidity as applied to natural water systems is the capacity of the water to neutralize OH^-. Acidic water is not frequently encountered, except in cases of severe pollution. Acidity generally results from the presence of weak acids such as $H_2PO_4^-$, CO_2, H_2S, proteins, fatty acids, and acidic metal ions, particularly Fe^{3+}. Acidity is more difficult to determine than is alkalinity. One reason for the difficulty in determining acidity is that two of the major contributors are CO_2 and H_2S, both volatile solutes that are readily lost from the sample. The acquisition and preservation of representative samples of water to be analyzed for these gases is difficult.

The term *free mineral acid* is applied to strong acids such as H_2SO_4 and HCl in water. Pollutant acid mine water contains an appreciable concentration of free mineral acid. Whereas total acidity is determined by titration with base to the phenolphthalein endpoint (pH 8.2, where both strong and weak acids are neutralized), free mineral acid is determined by titration with base to the methyl orange endpoint (pH 4.3, where only strong acids are neutralized).

The acidic character of some hydrated metal ions may contribute to acidity as shown by the following example:

$$Al(H_2O)_6^{3+} + H_2O \leftrightarrow Al(H_2O)_5OH^{2+} + H_3O^+ \quad (11.6.6)$$

For brevity in this book, the hydronium ion, H_3O^+, is abbreviated simply as H^+ and H^+-accepting water is omitted so that the above equation becomes

$$Al(H_2O)_6^{3+} \leftrightarrow Al(H_2O)_5OH^{2+} + H^+ \quad (11.6.7)$$

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Some industrial wastes, for example pickling liquor used to remove corrosion from steel, contain acidic metal ions and often some excess strong acid. For such wastes, the determination of acidity is important in calculating the amount of lime, or other chemicals, that must be added to neutralize the acid.

11.7 METAL IONS AND CALCIUM IN WATER

Metal ions in water, commonly denoted M^{n+}, exist in numerous forms. Despite what the formula implies, a bare metal ion, Mg^{2+} for example, cannot exist as a separate entity in water. To secure the highest stability of their outer electron shells, metal ions in water are bonded, or *coordinated*, to water molecules in forms such as the hydrated metal cation $M(H_2O)_x^{n+}$, or other stronger bases (electron-donor partners) that might be present. Metal ions in aqueous solution seek to reach a state of maximum stability through chemical reactions including acid-base,

$$Fe(H_2O)_6^{3+} \leftarrow \rightarrow FeOH(H_2O)_5^{2+} + H^+ \quad (11.7.1)$$

precipitation,

$$Fe(H_2O)_6^{3+} \leftarrow \rightarrow Fe(OH)_3(s)^{2+} + 3H_2O + 3H^+ \quad (11.7.2)$$

and oxidation-reduction reactions:

$$Fe(H_2O)_6^{2+} \leftarrow \rightarrow Fe(OH)_3(s) + 3H_2O + e^- + 3H^+ \quad (11.7.3)$$

These all provide means through which metal ions in water are transformed to more stable forms. Because of reactions such as these and the formation of dimeric species, such as $Fe_2(OH)_2^{4+}$, the concentration of simple hydrated $Fe(H_2O)_6^{3+}$ ion in water is vanishingly small; the same holds true for many other ionic species dissolved in water.

The properties of metals dissolved in water depend largely upon the nature of metal species dissolved in the water. Therefore, **speciation** of metals plays a crucial role in their environmental chemistry in natural waters and wastewaters. In addition to the hydrated metal ions, for example, $Fe(H_2O)_6^{3+}$ and hydroxo species such as $FeOH(H_2O)_5^{2+}$ discussed above, metals may exist in water reversibly bound to inorganic anions or to organic compounds as **metal complexes**, or they may be present as **organometallic** compounds containing carbon-to-metal bonds. The solubilities, transport properties, and biological effects of such species are often vastly different from those of the metal ions themselves. Subsequent sections of this chapter consider metal species with an emphasis upon metal complexes. Special attention is given to *chelation*, in which particularly strong metal complexes are formed.

Hydrated Metal Ions as Acids

Hydrated metal ions, particularly those with a charge of +3 or more, are Brönsted acids because they tend to lose H^+ in aqueous solution. The acidity of a metal ion increases with charge and decreases with increasing radius. Hydrated iron(III) ion is a relatively strong acid, ionizing as follows:

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$$Fe(H_2O)_6^{3+} \leftrightarrow Fe(H_2O)_5OH^{2+} + H^+ \quad (11.7.1)$$

Hydrated trivalent metal ions, such as iron(III), generally are minus at least one hydrogen ion at neutral pH values or above. Generally, divalent metal ions do not lose a hydrogen ion at pH values below 6, whereas monovalent metal ions such as Na^+ do not act as acids and exist in water solution as simple hydrated ions.

The tendency of hydrated metal ions to behave as acids may have a profound effect upon the aquatic environment. A good example is *acid mine water* (see Chapter 12, Section 12.8), which derives part of its acidic character from the tendency of hydrated iron(III) to lose H^+:

$$Fe(H_2O)_6^{3+} \leftrightarrow Fe(OH)_3(s) + 3H^+ + 3H_2O \quad (11.7.4)$$

Hydroxide, OH^-, bonded to a metal ion, may function as a bridging group to join two or more metals together as shown below for iron(III) that has lost H^+:

$$2Fe(H_2O)_5OH^{2+} \longrightarrow (H_2O)_4Fe\begin{matrix}H\\O\\O\\H\end{matrix}Fe(H_2O)_4^{4+} + 2H_2O \quad (11.7.5)$$

The process may continue with formation of higher hydroxy polymers terminating with precipitation of solid metal hydroxide.

Calcium and Hardness

Of the cations found in most freshwater systems, calcium generally has the highest concentration and often has the most influence on aquatic chemistry and water uses and treatment. The chemistry of calcium, although complicated enough, is simpler than that of the transition metal ions found in water. Calcium is a key element in many geochemical processes, and minerals constitute the primary sources of calcium ion in water. Among the primary contributing minerals are gypsum, $CaSO_4 \cdot 2H_2O$; anhydrite, $CaSO_4$; dolomite, $CaMg(CO_3)_2$; and calcite and aragonite, which are different mineral forms of $CaCO_3$.

Calcium is present in water as a consequence of equilibria between calcium and magnesium carbonate minerals and CO_2 dissolved in water, which it enters from the atmosphere and from decay of organic matter in sediments. These relationships are depicted in Figure 11.6. Water containing a high level of carbon dioxide readily dissolves calcium from its carbonate minerals:

$$CaCO_3(s) + CO_2(aq) + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^- \quad (11.7.6)$$

When the above reaction is reversed and CO_2 is lost from the water, calcium carbonate deposits are formed. The concentration of CO_2 in water determines the extent of dissolution of calcium carbonate. The carbon dioxide that water may gain by

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equilibration with the atmosphere is not sufficient to account for the levels of calcium dissolved in natural waters, especially groundwaters. Rather, the respiration of microorganisms degrading organic matter in water, sediments, and soil accounts for the high levels of CO_2 required to dissolve $CaCO_3$ in water. This is an extremely important factor in aquatic chemical processes and geochemical transformations.

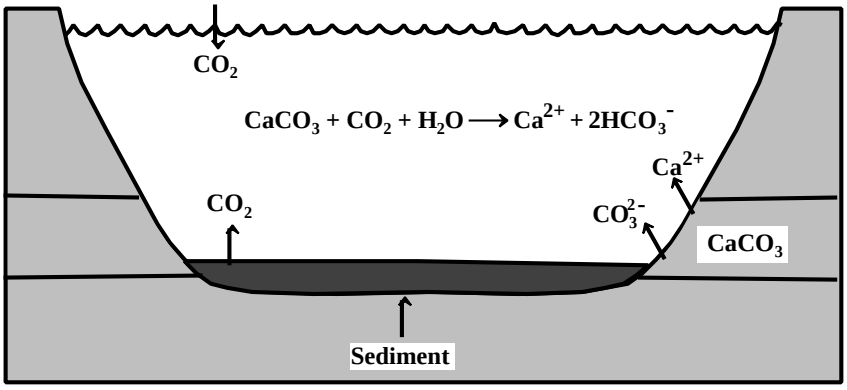


Figure 11.6 Carbon dioxide-calcium carbonate equilibria.

Calcium ion, along with magnesium and sometimes iron(II) ion, accounts for **water hardness**. The most common manifestation of water hardness is the curdy precipitate formed by the reaction of soap, a soluble sodium salt of a long-chain fatty acid, with calcium ion in hard water:

$$2C_{17}H_{33}COO^-Na^+ + Ca^{2+} \rightarrow Ca(C_{17}H_{33}CO_2)_2(s) + 2Na^+ \qquad (11.7.7)$$

Temporary hardness is due to the presence of calcium and bicarbonate ions in water and may be eliminated by boiling the water, thus causing the reversal of Equation 11.7.6:

$$Ca^{2+} + 2HCO_3^- \leftarrow\rightarrow CaCO_3(s) + CO_2(g) + H_2O \qquad (11.7.8)$$

Increased temperature may force this reaction to the right by evolving CO_2 gas, and a white precipitate of calcium carbonate may form in boiling water having temporary hardness.

11.8 OXIDATION-REDUCTION

Oxidation-reduction (redox) reactions in water involve the transfer of electrons between chemical species. In natural water, wastewater, and soil, most significant oxidation-reduction reactions are carried out by bacteria, so they are considered in this section as well.

The relative oxidation-reduction tendencies of a chemical system depend upon the activity of the electron, e^-. When the electron activity is relatively high, chemical species (even including water) tend to accept electrons

$$2H_2O + 2e^- \leftarrow\rightarrow H_2(g) + 2OH^- \qquad (11.8.1)$$

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and are reduced. When the electron activity is relatively low, the medium is **oxidizing**, and chemical species such as H_2O may be **oxidized**, losing electrons:

$$2H_2O \leftrightarrow O_2(g) + 4H^+ + 4e^- \quad (11.8.2)$$

The relative tendency toward oxidation or reduction is based upon the electrode potential, E, which is relatively more positive in an oxidizing medium and negative in a reducing medium (see Section 8.10). It is defined in terms of the half reaction,

$$2H^+ + 2e^- \leftrightarrow H_2 \quad (11.8.3)$$

for which E is defined as exactly zero when the activity of H^+ is exactly 1 (concentration approximately 1 mole per liter) and the pressure of H_2 gas is exactly 1 atmosphere. Because electron activity in water varies over many orders of magnitude, environmental chemists find it convenient to discuss oxidizing and reducing tendencies in terms of pE, a parameter analogous to pH ($pH = -\log a_{H^+}$) and defined conceptually as the negative log of the electron activity:

$$pE = -\log a_{e^-} \quad (11.8.4)$$

The value of pE is calculated from E by the relationship,

$$pE = \frac{E}{\frac{2.303RT}{F}} \quad (11.8.5)$$

where R is the gas constant, T is the absolute temperature, and *F* is the Faraday. At 25˚C for E in volts, $pE = E/0.0591$.

pE-pH Diagram

The nature of chemical species in water is usually a function of both pE and pH. A good example of this is shown by a simplified pE-pH diagram for iron in water, assuming that iron is in one of the four forms of Fe^{2+} ion, Fe^{3+} ion, solid $Fe(OH)_3$,or solid $Fe(OH)_2$ as shown in Figure 11.7. Water in which the pE is higher than that shown by the upper dashed line is thermodynamically unstable toward oxidation (Reaction 11.8.2), and below the lower dashed line water is thermodynamically unstable toward reduction (Reaction 11.8.3). It is seen that Fe^{3+} ion is stable only in a very oxidizing, acidic medium such as that encountered in acid mine water, whereas Fe^{2+} ion is stable over a relatively large region, as reflected by the common occurrence of soluble iron(II) in oxygen-deficient groundwaters. Highly insoluble $Fe(OH)_3$ is the predominant iron species over a very wide pE-pH range.

11.9 COMPLEXATION AND CHELATION

As noted in Section 11.7, metal ions in water are always bonded to water molecules in the form of hydrated ions represented by the general formula, $M(H_2O)_x^{n+}$, from which the H_2O is often omitted for simplicity. Other species may be present

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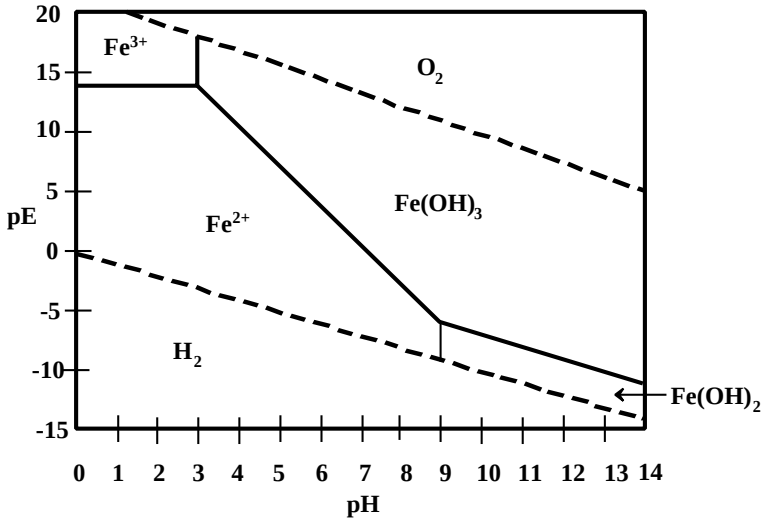


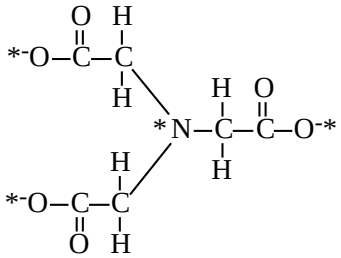
Figure 11.7 A simplified pE-pH diagram for iron in water (maximum total soluble iron concentration 1.0 x 10^{-5} M).

that bond to the metal ion more strongly than does water. Specifically, a metal ion in water may combine with an ion or compound that contributes electron pairs to the metal ion. Such a substance is an electron donor, or Lewis base. Called a **ligand**, it bonds to a metal ion to form a **complex** or **coordination compound** (or ion). Thus, cadmium ion in water combines with a cyanide ion ligand to form a complex ion, as shown below:

$$Cd^{2+} + CN^{-} \leftrightarrows CdCN^{+} \qquad (11.9.1)$$

Additional cyanide ligands can be added to form the progressively weaker (more easily dissociated) complexes with the chemical formulas $Cd(CN)_2$, $Cd(CN)_3^{-}$, and $Cd(CN)_4^{2-}$.

In this example, the cyanide ion is a **unidentate ligand**, which means that it possesses only one site that bonds to the cadmium metal ion. Complexes of unidentate ligands are of relatively little importance in solution in natural waters. Of considerably more importance are complexes with **chelating agents.** A chelating agent has more than one atom that can be bonded to a central metal ion at one time to form a ring structure. One such chelating agent is the nitrilotriacetate (NTA) ligand, which has the following formula:

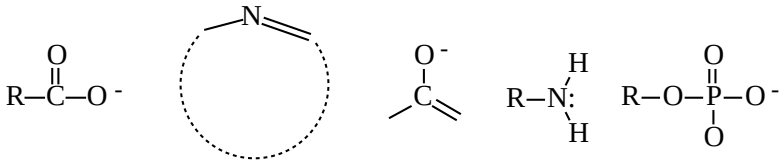


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This ion has four binding sites, each marked with an asterisk in the preceding illustration, which can simultaneously bond to a metal ion, forming a structure with three rings. Such a species is known as a **chelate**, and NTA is a **chelating** agent. In general, since a chelating agent may bond to a metal ion in more than one place simultaneously, chelates are more stable than complexes involving unidentate ligands. Stability tends to increase with the number of chelating sites available on the ligand.

Structures of metal chelates take a number of different forms, all characterized by rings in various configurations. The structure of a tetrahedrally coordinated chelate of nitrilotriacetate ion is shown in Figure 11.8.

The ligands found in natural waters and wastewaters contain a variety of functional groups which can donate the electrons required to bond the ligand to a metal ion. Among the most common of these groups are:



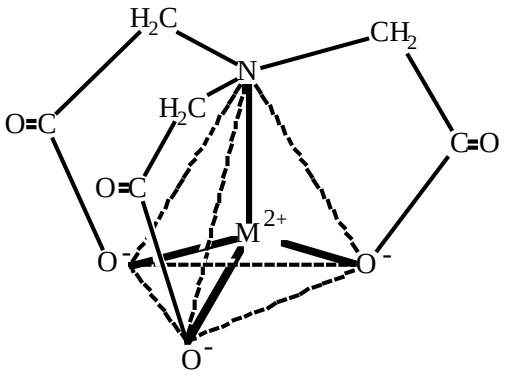


Figure 11.8 Nitrilotriacetate chelate of a divalent metal ion in a tetrahedral configuration.

These ligands complex most metal ions found in unpolluted waters and biological systems (Mg^{2+}, Ca^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Cu^{2+}, Zn^{2+}, VO^{2+}). They also bind to contaminant metal ions such as Co^{2+}, Ni^{2+}, Sr^{2+}, Cd^{2+}, and Ba^{2+}.

Complexation may have a number of effects, including reactions of both ligands and metals. Among the ligand reactions are oxidation-reduction, decarboxylation, and hydrolysis. Complexation may cause changes in oxidation state of the metal and may result in a metal becoming solubilized from an insoluble compound. The formation of insoluble complex compounds removes metal ions from solution. For example, complexation with negatively charged ligands can convert a soluble metal

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species from a cation to an anion, such as $Ni(CN)_4^{2-}$. Whereas cationic species are readily bound and immobilized by ion exchange processes in soil, anionic species are not strongly held by soil. Thus, codisposal of metal salts and chelating agents in wastes can result in increased hazards from heavy metals. On the other hand, some chelating agents are used for the treatment of heavy metal poisoning and insoluble chelating agents, such as chelating resins, can be used to remove metals from waste streams. Metal ions chelated by hazardous waste chelating agents, such as NTA from metal plating bath solutions, may be especially mobile in water.

Complex compounds and chelates of metals such as iron (in hemoglobin) and magnesium (in chlorophyll) are vital to life processes. Naturally occurring chelating agents, such as humic substances and amino acids, are found in water and soil. The high concentration of chloride ion in seawater results in the formation of some chloro complexes. Synthetic chelating agents such as sodium tripolyphosphate, sodium ethylenediaminetetraacetate (EDTA), sodium nitrilotriacetate (NTA), and sodium citrate are produced in large quantities for use in metal-plating baths, industrial water treatment, detergent formulations, and food preparation. Small quantities of these compounds enter aquatic systems through waste discharges.

Occurrence and Importance of Chelating Agents in Water

Chelating agents are common potential water pollutants. These substances can occur in sewage effluent and industrial wastewater such as metal plating wastewater. Chelates formed by the strong chelating agent ethylenediaminetetraacetate (EDTA) have been shown to greatly increase the migration rates of radioactive ^{60}Co from pits and trenches used for disposal of intermediate-level radioactive waste. EDTA was used as a cleaning and solubilizing agent for the decontamination of hot cells, equipment, and reactor components. Such chelates with negative charges are much less strongly sorbed by mineral matter and are vastly more mobile than the unchelated metal ions.

Complexing agents in wastewater are of concern primarily because of their ability to solubilize heavy metals from plumbing and from deposits containing heavy metals. Complexation may increase the leaching of heavy metals from waste disposal sites and reduce the efficiency with which heavy metals are removed with sludge in conventional biological waste treatment. Removal of chelated iron is difficult with conventional municipal water treatment processes. Iron(III) and perhaps several other essential micronutrient metal ions are kept in solution by chelation in algal cultures. The yellow-brown color of some natural waters is due to naturally occurring chelates of iron.

Complexation by Humic Substances

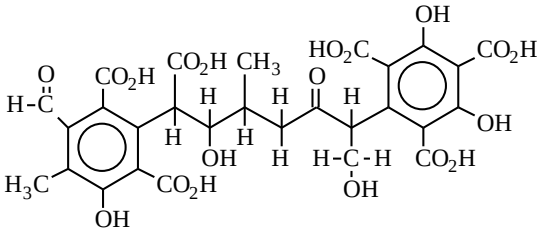
The most important class of complexing agents that occur naturally are the **humic substances.** These are degradation-resistant materials, formed during the decomposition of vegetation, that occur as deposits in soil, marsh sediments, peat, coal, lignite, or in almost any location where large quantities of vegetation have decayed. They are commonly classified on the basis of solubility. If a material containing humic substances is extracted with strong base, and the resulting solution

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is acidified, the products are (a) a nonextractable plant residue called **humin**; (b) a material that precipitates from the acidified extract, called **humic acid**; and (c) an organic material that remains in the acidified solution, called **fulvic acid**. Because of their acid-base, sorptive, and complexing properties, both the soluble and insoluble humic substances have a strong effect upon the properties of water. In general, fulvic acid dissolves in water and exerts its effects as the soluble species. Humin and humic acid remain insoluble and affect water quality through exchange of species, such as cations or organic materials, with water.

Humic substances are high-molecular-mass, polyelectrolytic macromolecules. Molecular masses range from a few hundred for fulvic acid to tens of thousands for the humic acid and humin fractions.

Some feeling for the nature of humic substances can be obtained by considering the following structure of a hypothetical molecule of fulvic acid:



The binding of metal ions by humic substances is one of the most important environmental qualities of humic substances. This binding can occur as chelation between a carboxyl group and a phenolic hydroxyl group, as chelation between two carboxyl groups, or as complexation with a carboxyl group (see below):

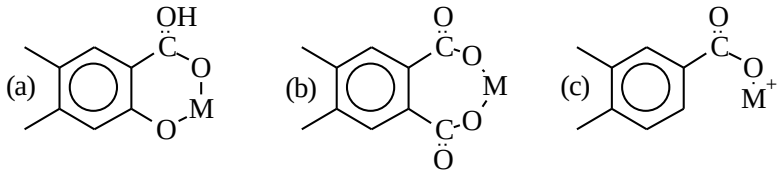


Figure 11.9 Binding of a metal ion, M^{2+}, by humic substances (a) by chelation between carboxyl and phenolic hydroxyl, (b) by chelation between two carboxyl groups, and (c) by complexation with a carboxyl group.

Soluble fulvic acid complexes of metals may be important in natural waters. They probably keep some of the biologically important transition-metal ions in solution and are particularly involved in iron solubilization and transport. Fulvic acid-type compounds are associated with color in water. These yellow materials, called **Gelbstoffe**, frequently are encountered along with soluble iron.

Insoluble humic substances, the humins and humic acids, effectively exchange cations with water and may accumulate large quantities of metals. Lignite coal, which is largely a humic-acid material, tends to remove some metal ions from water.

Special attention has been given to humic substances since about 1970, following the discovery of **trihalomethanes** (THMs, such as chloroform and dibromochloromethane) in water supplies. It is now generally believed that these suspected carcinogens can be formed in the presence of humic substances during the disinfection of raw municipal drinking water by chlorination (see Chapter 13). The

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humic substances produce THMs by reaction with chlorine. The formation of THMs can be reduced by removing as much of the humic material as possible prior to chlorination.

Metals Bound as Organometallic Compounds

Another major type of metal species important in hazardous wastes consists of **organometallic compounds**, which differ from complexes and chelates in that they are bonded to the metal by a carbon-metal bond and the organic ligand is frequently not capable of existing as a stable separate species. Typical examples of organometallic compound species are monomethylmercury ion and dimethylmercury:

Hg^{2+}	$Hg(CH_2)^+$	$Hg(CH_2)$
Mercury(II) ion	**Monomethylmercury ion**	**Dimethylmercury**

Organometallic compounds may enter the environment directly as pollutant industrial chemicals and some, including organometallic mercury, tin, selenium, and arsenic compounds, are synthesized biologically by bacteria. Some of these compounds are particularly toxic because of their mobilities in living systems and abilities to cross cell membranes.

11.10 WATER INTERACTIONS WITH OTHER PHASES

Most of the important chemical phenomena associated with water do not occur in solution, but rather through interaction of solutes in water with other phases. For example, the oxidation-reduction reactions catalyzed by bacteria occur in bacterial cells. Many organic hazardous wastes are carried through water as emulsions of very small particles suspended in water. Some hazardous wastes are deposited in sediments in bodies of water, from which they may later enter the water through chemical or physical processes and cause severe pollution effects.

Figure 11.10 summarizes some of the most significant types of interactions between water and other phases, including solids, immisicible liquids, and gases. Films of organic compounds, such as hydrocarbon liquids, may be present on the surface of water. Exposed to sunlight, these compounds are subject to photochemical reactions (see Section 16.4). Gases such as O_2 , CO_2, CH_4, and H_2S are exchanged with the atmosphere. Photosynthesis occurs in suspended cells of algae, and other biological processes, such as biodegradation of organic wastes, occur in bacterial cells. Particles contributing to the turbidity of water may be introduced by physical processes, including the erosion of streams or sloughing of water impoundment banks. Chemical processes, such as the formation of solid $CaCO_3$ illustrated in Figure 11.10, may also form particles in water.

Sediments

Sediments bind a wide variety of chemical species and are sites of many chemical and biochemical processes. Anaerobic fermentation of organic matter by bacteria produces methane gas evolved from sediments, along with CO_2 and, fre-

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quently, H_2S. Similar bacteria produce mobile $HgCH_3^+$ and $Hg(CH_3)_2$ from insoluble, relatively harmless inorganic mercury compounds. Sediments are sinks for many hazardous organic compounds and heavy metal salts that have gotten into water.

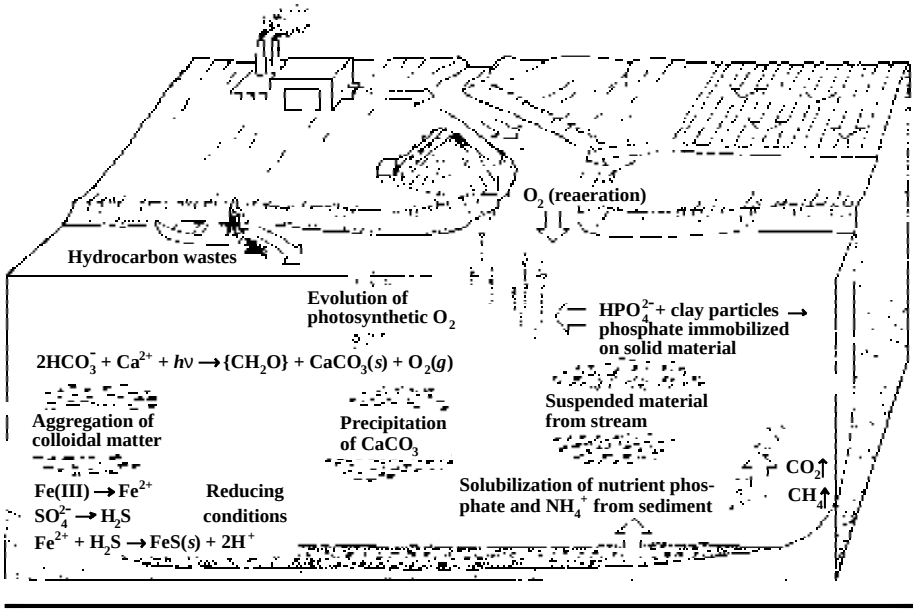


Figure 11.10 Aquatic chemical processes at interfaces between water and gases, solids, or other liquids.

Colloids

The most important interactions between species dissolved in aqueous solution and species in other phases occur with **colloidal particles** ranging from 0.001 micrometer (μm) to 1 μm in diameter and suspended in water, enabling maximum exposure to the water and solutes dissolved in it. Colloids have a strong influence on aquatic chemistry. Because of their extremely small size, these particles have a very high surface-to-volume ratio. Toxic substances in colloidal form are much more available to organisms in water than they are in bulk form. Special measures are required to remove colloidal particles from water. Usually, chemical treatment measures are applied to cause colloidal particles to aggregate together (processes called **coagulation** or **flocculation**), and the solids are removed by filtration.

11.11 AQUATIC LIFE

The living organisms (**biota**) in an aquatic ecosystem can be classified as either autotrophic or heterotrophic. **Autotrophic** biota utilize solar or chemical energy to fix elements from simple, nonliving inorganic material into complex life molecules that compose living organisms. Autotrophic organisms that utilize solar energy to synthesize organic matter from inorganic materials are called **producers**.

Heterotrophic organisms utilize the organic substances produced by autotrophic organisms for energy and as raw materials for the synthesis of their own biomass.

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Decomposers (or **reducers**) are a subclass of the heterotrophic organisms and consist of chiefly bacteria and fungi, which ultimately break down material of biological origin to the simple compounds originally fixed by the autotrophic organisms.

Microorganisms in Water

Microorganisms compose a diverse group of organisms generally capable of existing as single cells that can be seen only under a microscope. Microscopically small single-celled microorganisms, consisting of bacteria, fungi, and algae are of the utmost importance in water for a number of reasons as listed below:

- Through their ability to fix inorganic carbon, algae and photosynthetic bacteria are the predominant producers of the biomass that supports the rest of the food chain in bodies of water.
- As catalysts of aquatic chemical reactions, bacteria mediate most of the significant oxidation-reduction processes that occur in water.
- By breaking down biomass and mineralizing essential elements, especially nitrogen and phosphorus, aquatic microorganisms play a key role in nutrient cycling.
- Aquatic microorganisms are essential for the major biogeochemical cycles.
- Aquatic bacteria are responsible for the breakdown and detoxification of many xenobiotic pollutants that get into the hydrosphere.

From the viewpoint of environmental chemistry, the small size of microorganisms is particularly significant because it gives them a very high surface/volume ratio, enabling very rapid exchange of nutrients and metabolic products with their surroundings, and resulting in exceptionally high rates of metabolic reactions. This, combined with the spectacularly fast geometric increase in population of single-celled microorganisms by fission during the log phase of growth (see discussion of bacterial growth rates later in this chapter and Figure 11.12) enables microganisms to multiply very rapidly on environmental chemical substrates, such as biodegradable organic matter.

Microorganisms function as living catalysts that enable a vast number of chemical processes to occur in water and soil. Most of the important chemical reactions that take place in water and soil, particularly those involving organic matter and oxidation-reduction processes, occur through bacterial intermediaries. Algae are the primary producers of biological organic matter (biomass) in water. Microorganisms are responsible for the formation of many sediment and mineral deposits; they also play the dominant role in secondary wastewater treatment. Pathogenic microorganisms must be eliminated from water purified for domestic use.

Algae

For the purposes of discussion here, **algae** can be considered as generally microscopic organisms that subsist on inorganic nutrients and produce organic matter from

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carbon dioxide by photosynthesis. In a highly simplified form, the production of organic matter by algal photosynthesis is described by the reaction

$$CO_2 + H_2O \xrightarrow{h\nu} \{CH_2O\} + O_2(g) \qquad (11.11.1)$$

where $\{CH_2O\}$ represents a unit of carbohydrate and $h\nu$ stands for the energy of a quantum of light.

Fungi

Fungi are nonphotosynthetic organisms. The morphology (structure) of fungi covers a wide range, and is frequently manifested by filamentous structures. Discovered in 1992, the largest and oldest organism known (as verified by DNA analysis) is a huge fungus covering about 40 acres of northern Michigan forest land. Fungi are aerobic (oxygen-requiring) organisms and generally tolerate more-acidic media and higher concentrations of heavy metal ions than bacteria.

Although fungi do not grow well in water, they play an important role in determining the composition of natural waters and wastewaters because of the large amount of their decomposition products that enter water from the breakdown of cellulose in wood and other plant materials. To accomplish this, fungal cells secrete an extracellular enzyme (exoenzyme), *cellulase*. An environmentally important byproduct of fungal decomposition of plant matter is humic material (Section 11.9), which interacts with hydrogen ions and metals.

11.12 BACTERIA

Bacteria are single-celled prokaryotic microorganisms shaped as rods (**bacillus**), spheres (**coccus**), or spirals (**vibrios**, **spirilla**, **spirochetes**) that are uniquely important in environmental chemistry. Characteristics of most bacteria include a semirigid cell wall, motility with flagella for those capable of movement, unicellular nature (although clusters of cloned bacterial cells are common), and multiplication by binary fission in which each of two daughter cells is genetically identical to the parent cell.

Bacteria obtain the energy and raw materials needed for their metabolic processes and reproduction by mediating chemical reactions. Nature provides a large number of such reactions, and bacterial species have evolved that utilize many of them. Because of their participation in such reactions, bacteria are involved in many biogeochemical processes and elemental transitions and cycles in water and soil.

The metabolic activity of bacteria is greatly influenced by their small size, which is of the order of a micrometer in magnitude. Their surface-to-volume ratio is very large, so that the inside of a bacterial cell is highly accessible to a chemical substance in the surrounding medium. Thus, for the same reason that a finely divided catalyst is more efficient than a more coarsely divided one, bacteria may bring about very rapid chemical reactions compared with those mediated by larger organisms.

An example of autotrophic bacteria is *Gallionella*, which, like all autotrophic bacteria, employs inorganic carbon as a carbon source and derives its energy from mediating a chemical reaction:

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$$4FeS(s) + 9O_2 + 10H_2O \rightarrow 4Fe(OH)_3(s) + 4SO_4^{2-} + 8H^+ \quad (11.12.1)$$

Because they consume and produce a wide range of minerals, autotrophic bacteria are involved in many geochemical transformations.

Heterotrophic bacteria are much more common in occurrence than autotrophic bacteria. They are primarily responsible for the breakdown of pollutant organic matter in water and of organic wastes in biological waste-treatment processes.

Aerobic bacteria require molecular oxygen as an electron receptor:

$$O_2 + 4H^+ + 4e^- \rightarrow H_2O \quad (11.12.2)$$

Anaerobic bacteria function only in the complete absence of molecular oxygen, using substances such as nitrate ion and sulfate ion as substitutes for O_2. Frequently, molecular oxygen is quite toxic to anaerobic bacteria. A third class of bacteria, **facultative bacteria**, utilize free oxygen when it is available and use other substances as electron receptors (oxidants) when molecular oxygen is not available.

The Prokaryotic Bacterial Cell

Unicellular bacteria and cyanobacteria consist of prokaryotic cells, which differ in several major respects from the eukaryotic cells of higher organisms. Illustrated in Figure 11.11, prokaryotic bacterial cells are enclosed in a **cell wall**, which in many bacteria is frequently surrounded by a **slime layer** (capsule). The thin **cell membrane** or **cytoplasmic membrane** on the inner surface of the cell wall encloses the cellular cytoplasm, controls the nature and quantity of materials transported into and out of the cell, and is susceptible to damage from some toxic substances. Hairlike **pili**

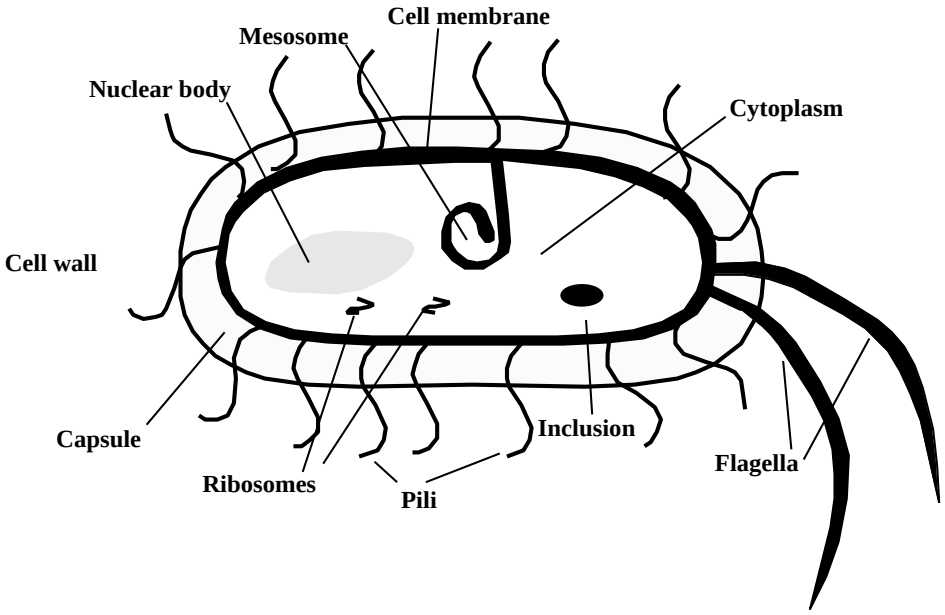


Figure 11.11 Generic prokaryotic bacterial cell illustrating major cell features.

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on the surface of a bacterial cell enable the cell to stick to surfaces. **Flagella** are movable appendages that enable motile bacterial cells to move by their whipping action. Bacterial cells are filled with **cytoplasm**, an aqueous solution and suspension containing proteins, lipids, carbohydrates, nucleic acids, ions, and other materials constituting the medium in which the cell's metabolic processes are carried out. The major constituents of cytoplasm are: a **nuclear body** composed of a single DNA macromolecule that controls metabolic processes and reproduction; **inclusions** of reserve food material, usually consisting of fats and carbohydrates; and **ribosomes**, which function as sites of protein synthesis.

Rate of Bacterial Growth

The population size of bacteria and unicellular algae as a function of time in a growth culture is illustrated by Figure 11.12, which shows a **population curve** for a bacterial culture. Such a culture is started by inoculating a rich nutrient medium with a small number of bacterial cells. Bacteria multiply exponentially in the log phase.

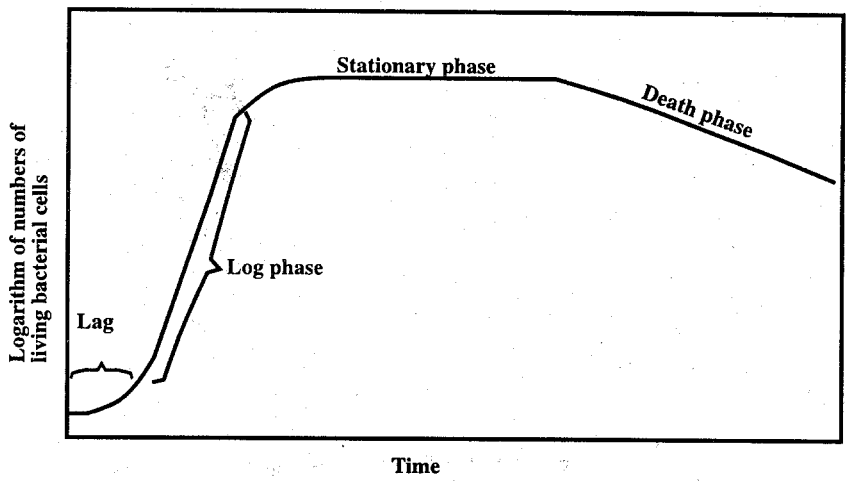


Figure 11.12 Population curve for a bacterial culture.

Bacterial Metabolism

Metabolic reactions by which bacteria break down substances and extract energy, as well as synthesizing biological materials, are mediated by enzymes (see Chapter 10). Figure 11.13 illustrates the effect of **substrate concentration** on enzyme activity. It is seen that enzyme activity increases in a linear fashion up to a value that represents saturation of the enzyme activity. Beyond this concentration, increasing substrate levels do not result in increased enzyme activity. This kind of behavior is reflected in bacterial activity and growth, which increase with available nutrients up to a saturation value. Superimposed on this plot in a bacterial system is increased bacterial population, which, in effect, increases the amount of available enzyme.

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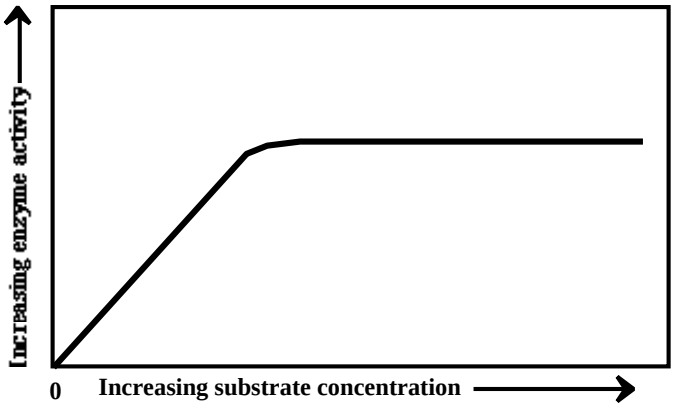


Figure 11.13 Effect of increasing substrate concentration on enzyme activity.

Figure 11.14 shows that a plot of bacterial enzyme activity as a function of temperature exhibits a maximum growth rate at an optimum temperature that is skewed toward the high temperature end of the curve. The abrupt dropoff beyond the temperature maximum occurs because enzymes are destroyed by being denatured at temperatures not far above the optimum. The temperature for optimum growth rate varies with the kind of bacteria.

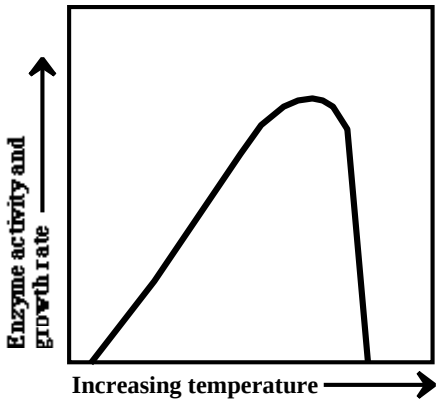


Figure 11.14 Enzyme activity as a function of temperature. A plot of bacterial growth versus temperature has the same shape.

Figure 11.15 is a plot of enzyme activity versus pH. The optimum pH may vary somewhat; for example, bacteria that are responsible for generating acid mine water (see Section 12.8) have enzymes with optimum pHs that are very low. In general, though, enzymes typically have a pH optimum around neutrality. Enzymes tend to become denatured at pH extremes. This behavior likewise is reflected in plots of bacterial metabolism as a function of pH. For some bacteria that thrive in acid, such as those that generate sulfuric acid by the oxidation of sulfide or organic acids by fermentation processes, the optimum pH may be quite low.

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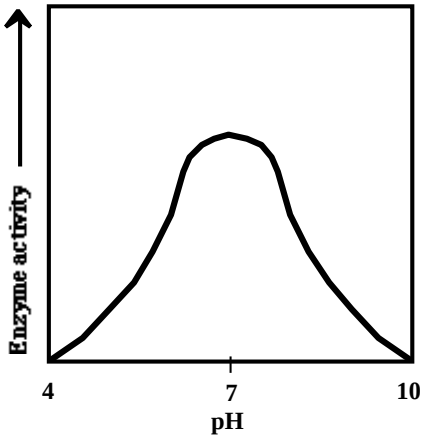


Figure 11.15 Enzyme activity as a function of pH.

11.13 MICROBIALLY MEDIATED ELEMENTAL TRANSISTIONS AND CYCLES

Microbially mediated transitions between elemental species and the elemental cycles resulting therefrom constitute one of the most significant aspects of geochemistry as influenced by biological processes. Such cycles involving organisms—predominantly microorganisms—are called biogeochemical cycles. This section addresses biogeochemical cycles for several important elements.

Microbial Transformations of Carbon

The carbon cycle is represented in Figure 11.16. A relatively small, but highly significant, portion of global carbon is in the atmosphere as CO_2. A very large amount of carbon is present as minerals, particularly calcium and magnesium carbonates. Another fraction of carbon is fixed as petroleum and natural gas, with a much larger amount as hydrocarbonaceous kerogen, coal, and lignite. Manufacturing processes are used to convert hydrocarbons to xenobiotic compounds with functional groups containing halogens, oxygen, nitrogen, phosphorus, or sulfur. Though a very small amount of total environmental carbon, these compounds are particularly significant because of their toxicological chemical effects.

Microorganisms are strongly involved in the carbon cycle, mediating crucial biochemical reactions discussed later in this section. Photosynthetic algae are the predominant carbon-fixing organisms in water; as they consume CO_2, the pH of the water is raised enabling precipitation of $CaCO_3$ and $CaCO_3 \cdot MgCO_3$. Organic carbon fixed by microorganisms is transformed by biogeochemical processes to fossil petroleum, kerogen, coal, and lignite. Microorganisms degrade organic carbon from biomass, petroleum, and xenobiotic sources, ultimately returning it to the atmosphere as CO_2. The following summarize the prominent ways in which microorganisms are involved in the carbon cycle:

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- **Photosynthesis** in which algae, higher plants, and photosynthetic bacteria use light energy to fix inorganic carbon in a high-energy organic form:

 $CO_2 + H_2O \xrightarrow{h\nu} \{CH_2O\} + O_2(g)$

- **Respiration** in which organic matter is oxidized in the presence of molecular O_2 (**aerobic respiration**)

 $\{CH_2O\} + O_2(g) \rightarrow CO_2 + H_2O$

 or **anaerobic respiration**, which uses oxidants other than O_2, such as NO_3^- or SO_4^{2-}.

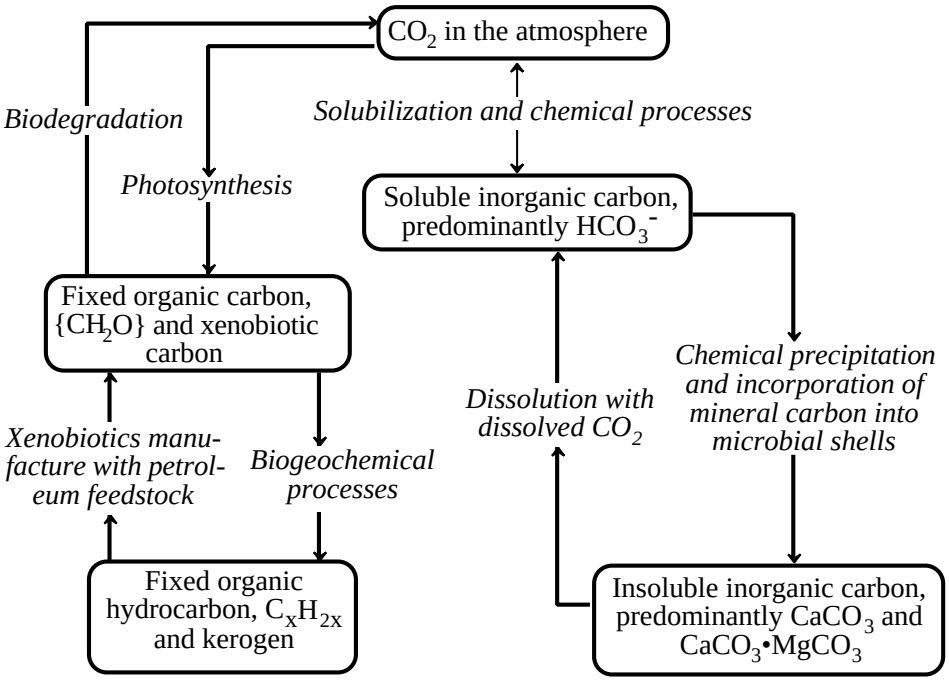


Figure 11.16 Important aspects of the biogeochemical carbon cycle.

- **Degradation of biomass** by bacteria and fungi. Biodegradation of dead organic matter consisting predominantly of plant residues prevents accumulation of excess waste residue and converts organic carbon, nitrogen, sulfur, and phosphorus to simple organic forms that can be utilized by plants. It is a key part of the biogeochemical cycles of these elements and also leaves a humus residue that is required for optimum physical condition of soil.
- **Methane production** by methane-forming bacteria, such as *Methanobacterium*, in anoxic (oxygen-less) sediments,

 $2\{CH_2O\} \rightarrow CH_4 + CO_2$

 plays a key role in local and global carbon cycles as the final step in the anaerobic decomposition of organic matter. It is the source of about 80%

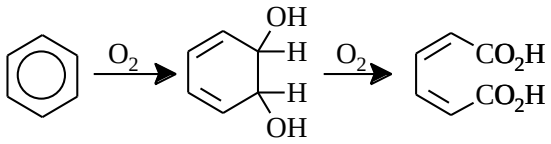
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of the methane entering the atmosphere. Microbial methane production is a **fermentation reaction**, defined as an oxidation-reduction process in which both the oxidizing agent and reducing agent are organic substances.

- **Bacterial utilization and degradation of hydrocarbons.** The oxidation of higher hydrocarbons under aerobic conditions by *Micrococcus*, *Pseudomonas*, *Mycobacterium*, and *Nocardia* is an important environmental process by which petroleum wastes are eliminated from water and soil. The initial step in the microbial oxidation of alkanes is conversion of a terminal $-CH_3$ group to a $-CO_2$ group followed by β–oxidation,

 $$CH_3CH_2CH_2CH_2CH_2O_2H + 3O_2 \rightarrow CH_3CH_2CH_2O_2H + 2CO_2 + 2H_2O$$

 wherein carbon atoms are removed in 2-carbon fragments. The overall process leading to ring cleavage in aromatic hydrocarbons is the following in which cleavage is preceded by addition of –OH to adjacent carbon atoms:

- **Biodegradation of organic matter**, such as occurs in treatment of municipal wastewater by reactions represented in a general sense by,

 $$\{CH_2O\} + O_2(g) \rightarrow CO_2 + H_2O + \text{biomass}$$

Microbial Transformations of Nitrogen

Some of the most important microorganism-mediated chemical reactions in aquatic and soil environments are those involving nitrogen compounds. They are key constituents of the **nitrogen cycle** shown in Figure 11.17, a cycle that describes the dynamic processes through which nitrogen is interchanged among the atmosphere, organic matter, and inorganic compounds. The key microbially mediated processes in the nitrogen cycle are the following:

- **Nitrogen fixation**, the binding of atmospheric nitrogen in a chemically combined form:

 $$3\{CH_2O\} + 2N_2 + 3H_2O + 4H^+ \rightarrow 3CO_2 + 4NH_4^+$$

 Biological nitrogen fixation is a key biochemical process in the environment and is essential for plant growth in the absence of synthetic fertilizers.

- **Nitrification**, the conversion of N(-III) to N(V) catalyzed by *Nitrosomonas* and *Nitrobacter*:

 $$2O_2 + NH_4^+ \rightarrow NO_3^- + 2H^+ + H_2O$$

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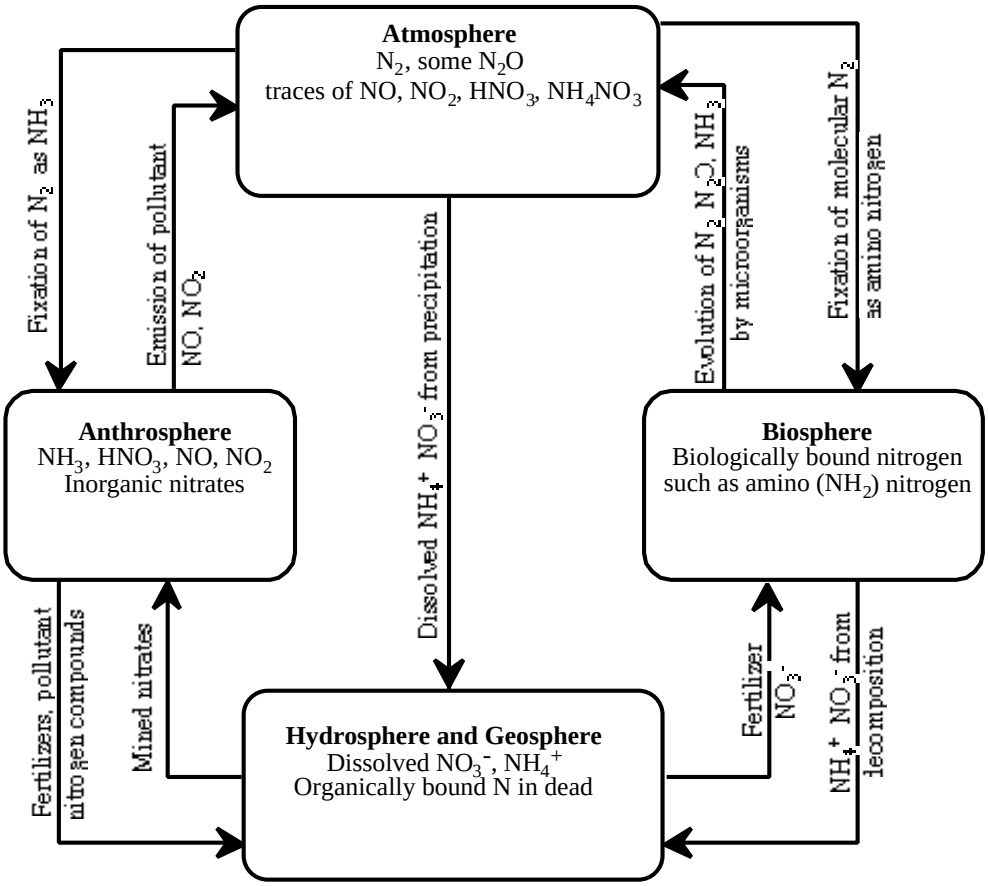


Figure 11.17 Aspects of the nitrogen cycle.

Nitrification is especially important in nature because nitrogen is absorbed by plants primarily as nitrate ion, which is produced by nitrification. When fertilizers are applied in the form of ammonium salts or anhydrous ammonia, a microbial transformation to nitrate enables maximum assimilation of nitrogen by the plants.

- **Nitrate reduction** by which nitrogen in chemical compounds is reduced by microbial action to lower oxidation states in the absence of free oxygen:

 $$2NO_3^- + \{CH_2O\} \rightarrow 2NO_2^- + H_2O + CO_2$$

 $$2NO_2^- + 3\{CH_2O\} + 4H^+ \rightarrow 2NH_4^+ + 3CO_2 + H_2O$$

- **Denitrification**, which produces N_2 gas from chemically fixed nitrogen:

 $$4NO_3^- + 5\{CH_2O\} + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O$$

 Denitrification is the mechanism by which fixed nitrogen is returned to the atmosphere and is useful in advanced water treatment for the removal of

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nutrient nitrogen. Loss of nitrogen to the atmosphere may also occur through the formation of N_2O and NO by bacterial action on nitrate and nitrite catalyzed by several types of bacteria.

Microbial Transformations of Sulfur

The sulfur cycle involves interconversions among a number of sulfur species, including inorganic soluble sulfates, insoluble sulfates, soluble sulfide, gaseous hydrogen sulfide, and insoluble sulfides; biologically bound sulfur; and sulfur in synthetic organic compounds. The major microbially mediated processes in this cycle are the following:

- **Sulfate reduction** to sulfide by bacteria such as *Desulfovibrio*, which utilizes sulfate as an electron acceptor in the oxidation of organic matter:

 $$SO_4^{2-} + 2\{CH_2O\} + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O$$

 The odiferous and toxic H_2S product may cause serious problems with water quality.

- **Sulfide oxidation** by bacteria such as *Thiobacillus*:

 $$2H_2S + 4O_2 \rightarrow 4H^+ + 2SO_4^{2-}$$

 Oxidation of sulfur in a low oxidation state to sulfate ion produces sulfuric acid, a strong acid. Some of the bacteria that mediate this reaction, such as *Thiobacillus thiooxidans* are remarkably acid tolerant. Acid-tolerant sulfur-oxidizing bacteria produce and thrive in acidic waters, such as acid mine water, which can be very damaging to the environment.

- **Degradation of organic sulfur compounds** by bacterially mediated processes that can result in production of strong-smelling noxious volatile organic sulfur compounds, such as methyl thiol, CH_3SH, and dimethyl disulfide, CH_3SSCH_3. The formation of these compounds, in addition to that of H_2S, accounts for much of the odor associated with the biodegradation of sulfur-containing organic compounds. Hydrogen sulfide is formed from a large variety of organic compounds through the action of a number of different kinds of microorganisms.

Microbial Transformations of Phosphorus

The phosphorus cycle involves natural and pollutant sources of phosphorus including biological, organic, and inorganic phosphorus. Biological phosphorus is a key constituent of cellular DNA. Organic phosphorus occurs in organophosphate insecticides. The major inorganic phosphorus species are soluble $H_2PO_4^-$ and HPO_4^{2-} and insoluble $Ca_5(OH)(PO_4)_3$. Soil and aquatic microbial processes are very important in the phosphorus cycle. Of particular importance is the fact that phosphorus is the most common limiting nutrient in water, particularly for the growth of algae. Bacteria are even more effective than algae in taking up phosphate from water, accumulating it as excess cellular phosphorus that can be released to

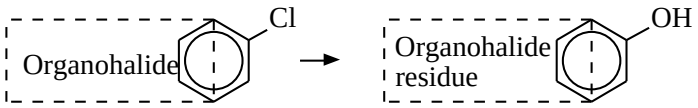
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support additional bacterial growth, if the supply of phosphorus becomes limiting. Microorganisms that die release phosphorus that can support the growth of additional organisms.

Biodegradation of phosphorus compounds is important in the environment for two reasons. The first of these is that it is a *mineralization* process that releases inorganic phosphorus from the organic form. This process provides an important source of nutrient orthophosphate required for the growth of plants and algae. Second, biodegradation deactivates highly toxic organophosphate compounds, such as the organophosphate insecticides.

Microbial Transformations of Halogens and Organohalides

Among the more important microbial processes that operate on pollutant xenobiotic compounds in soil and water are those involving the degradation of organohalide compounds. Such compounds, particularly the organochloride compounds, are among the more abundant air and water pollutants and hazardous waste constituents. Some are relatively toxic and even carcinogenic, and they tend to accumulate in lipid tissues. The key step in biodegradation of organohalide compounds is **dehalogenation**, which involves the replacement of a halogen atom:



Microbial Transformations of Iron

Some bacteria, including *Ferrobacillus*, *Gallionella*, and some forms of *Sphaerotilus*, utilize iron compounds in obtaining energy for their metabolic needs, by oxidizing iron(II) to iron(III) with molecular oxygen:

$$4Fe(II) + 4H^+ + O_2 \rightarrow 4Fe(III) + 2H_2O \qquad (11.13.1)$$

The carbon source for some of these bacteria is CO_2. Since they do not require organic matter for carbon, and because they derive energy from the oxidation of inorganic matter, these bacteria may thrive in environments where organic matter is absent. The iron(III) product is amassed as large quantities of solid $Fe(OH)_3$, so that large deposits of hydrated iron(III) oxide form in areas where iron-oxidizing bacteria thrive. Some of the iron bacteria, notably *Gallionella*, secrete large quantities of hydrated iron(III) oxide in the form of intricately branched structures that grow at the end of a twisted stalk of the iron oxide.

Acid Mine Waters

One consequence of bacterial action on metal compounds is acid mine drainage, a common and damaging water pollution problem. Acid mine water results from the presence of sulfuric acid produced by the oxidation of pyrite, FeS_2. Microorganisms are closely involved in the overall process, which consists of several reactions. Acid mine water is discussed further in Section 12.7.

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CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

The most important unique properties of water that largely determine its environmental chemical behavior are [1]_____ Thermal stratification of bodies of water results from water's [2]_____ _____. Most of the many oxidation-reduction reactions that occur in water are mediated by bacteria [3]_____. The ability of solutes in water to neutralize added strong acid is called [4]_____ and water hardness is due mostly to the presence of [5]_____. In water near neutral pH the major contributor to alkalinity is [6]_____. A major pollutant contributor to acidity is free mineral acid manifested by the presence of [7]_____ _____. The hydronium ion, H_3O^+, indicates [8]_____, and can be abbreviated simply as [9]_____. A bare metal ion cannot exist as a separate entity in water, but is present instead as [10]_____. Because they tend to lose H^+ in aqueous solution, hydrated metal ions with a charge of +3 or more, act as [11]_____. Calcium is present in water as a consequence of [12]_____ _____.The reaction $2C_{17}H_{33}COO^-Na^+ + Ca^{2+} \rightarrow Ca(C_{17}H_{33}CO_2)_2(s) + 2Na^+$ is a manifestation of [13]_____. Oxidation-reduction reactions in water involve [14]_____ _____, and in natural water, wastewater, and soil are carried out by [15]_____. The relative oxidation-reduction tendencies of a chemical system depend upon [16]_____. The parameter pE is defined conceptually as [17]_____. In the pE-pH diagram for iron in water, the species that predominates at low pE and low pH is [18]_____, whereas at high pE and higher pH it is [19]_____. In the pE-pH diagram, the upper and lower dashed lines show [20]_____ _____, respectively. A ligand bonds to a metal ion to form a [21]_____. The NTA anion as a ligand has [22]_____ binding sites, and it forms chelates with [23]_____ rings. Some of the more significant environmental effects of complexation and chelation are. [24]_____ _____. Complexing agents in wastewater are of concern primarily because of [25]_____ _____. The most important class of complexing agents that occur naturally are, [26]_____, which are [27]_____ _____. These substances are divided into the three classes of [28]_____ and are commonly divided on the basis of [29]_____.They are most significant in drinking water supplies because of [30]_____ _____. Organometallic compounds, differ from

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complexes and chelates in that [31]_____
_____.
Most of the important chemical phenomena associated with water do not occur in solution, but rather through [32]_____,
which may include [33]_____.
Sediments are [34]_____
_____ and the site of [35]_____.
Very small particles ranging from 0.001 micrometer (μm) to 1 μm in diameter have a very high surface-to-volume ratio and are called [36]_____.
Living organisms that utilize solar or chemical energy to fix elements from simple, nonliving inorganic material into complex life molecules that compose living organisms are called [37]_____, whereas heterotrophic organisms [38]_____
_____. Four reasons that microorganisms are especially important in water are [39]_____

The small size of microorganisms is particularly significant because [40]_____
_____. In a simplified sense the basic reaction by which algae produce biomass is [41]_____.
Fungi are important in the environmental chemistry of water because [42]_____

_____. Three classifications of bacteria based upon their requirement for oxygen are [43]_____.
The kinds of cells that bacteria have are [44]_____.
The major phases in a bacterial growth curve are [45]_____
_____.
A plot of bacterial enzyme activity as a function of temperature is shaped such that it [46]_____

_____ because [47]_____

_____. The prominent ways in which microorganisms are involved in the carbon cycle are [48]_____

_____. The steps in the nitrogen cycle that involve bacteria are [49]_____.
Microbial transformations of sulfur involve [50]_____

_____. The two reasons for which biodegradation of phosphorus compounds is important in the environment are [51]_____
_____.
The key step in biodegradation of organohalide compounds is [52]_____.

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The bacterially-catalyzed oxidation of iron(II) to iron(III) by bacteria can result in the formation of large deposits of [53]_____. Acid mine water results from the presence of [54]_____ produced by the oxidation of [55]_____ _____.

Answers to Chapter Summary

1. Properties of water as listed in Table 11.1.
2. unique temperature-density relationship
3. bacteria
4. alkalinity
5. Ca^{2+} ion
6. HCO_3^- ion
7. strong acids such as H_2SO_4 and HCl in water
8. H^+ ion bound to H_2O
9. H^+
10. the hydrated metal cation $M(H_2O)_x^{n+}$
11. Brönsted acids
12. equilibria between calcium and magnesium carbonate minerals and CO_2 dissolved in water
13. water hardness
14. the transfer of electrons between chemical species
15. bacteria
16. the activity of the electron e^-
17. the negative log of the electron activity
18. Fe^{2+}
19. solid $Fe(OH)_3$
20. the oxidizing and reducing limits of water stability
21. complex or coordination compound
22. four
23. three
24. reactions of both ligands and metals, changes in oxidation state of the metal, and effects on life processes.
25. their ability to solubilize heavy metals
26. humic substances
27. degradation-resistant materials formed during the decomposition of vegetation
28. fulvic acid, humic acid, and humin
29. solubility, particularly in acid and base
30. their potential to form trihalomethanes
31. the organic portion is bonded to the metal by a carbon-metal bond and the organic ligand is frequently not capable of existing as a stable separate species
32. interaction of solutes in water with other phases
33. solids, immisicible liquids, and gases
34. repositories of a wide variety of chemical species
35. many chemical and biochemical processes
36. colloids
37. autotrophic organisms

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38. utilize the organic substances produced by autotrophic organisms as energy sources and as the raw materials for the synthesis of their own biomass
39. They are the predominant producers of the biomass in water, they mediate most of the significant oxidation-reduction processes that occur in water, they play a key role in nutrient cycling, they are essential for the major biogeochemical cycles, and they are responsible for the breakdown and detoxication of many xenobiotic pollutants that get into the hydrosphere.
40. it gives them a very high surface/volume ratio
41. $CO_2 + H_2O \xrightarrow{h\nu} \{CH_2O\} + O_2(g)$
42. they play an important role in determining the composition of natural waters and wastewaters due to the large amount of their decomposition products that enter water from the breakdown of cellulose in wood and other plant materials
43. aerobic, anaerobic, and facultative
44. prokaryotic cells
45. lag phase, log phase, stationary phase, and death phase
46. exhibits a maximum growth rate at an optimum temperature that is skewed toward the high temperature end of the curve
47. enzymes are destroyed by being denatured at temperatures not far above the optimum
48. photosynthesis, respiration, degradation of biomass, methane production, bacterial utilization and degradation of hydrocarbons, and biodegradation of organic matter
49. nitrogen fixation, nitrification, nitrate reduction, and denitrification
50. sulfate reduction, sulfide oxidation, and biodegradation of organic sulfur compounds
51. mineralization, which releases inorganic phosphorus from the organic form, and deactivation of highly toxic organophosphate compounds
52. dehalogenation
53. iron(III) hydroxide
54. sulfuric acid
55. pyrite, FeS_2

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QUESTIONS AND PROBLEMS

1. A sample of groundwater heavily contaminated with soluble inorganic iron is brought to the surface and the alkalinity is determined without exposing the sample to the atmosphere. Why does a portion of such a sample exposed to the atmosphere for some time exhibit a decreased alkalinity?
2. What indirect role is played by bacteria in the formation of limestone caves?
3. Over the long term, irrigation must be carried out so that there is an appreciable amount of runoff, although a much smaller quantity of water would be sufficient to wet the ground. Why must there be some runoff?
4. Of the following, the true statement is that the specific species H_2CO_3 (a) is the predominant form of CO_2 dissolved in water; (b) exists only at pH values above 9; (c) makes up only a small fraction of CO_2 dissolved in water, even at low pH; (d) is not known to exist at all; (e) is formed by the reaction between CO_2 and OH^-.
5. Although algae release oxygen by photosynthesis, why may oxygen levels become rather low at night in water supporting a heavy growth of algae?
6. Alkalinity is **not** (a) a measure of the degree to which water can support algal growth, (b) the capacity of water to neutralize acid, (c) a measure of the capacity of water to resist a decrease in pH, (d) a direct measure of pH, (e) important in considerations of water treatment.
7. What is the molar concentration of O_2 in water in equilibrium with atmospheric air at 25˚C?

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8. Explain why a solution of $Fe_2(SO_4^{2-})_3$ in water is acidic.
9. How does the ionic radius of ions such as Ca^{2+}, Fe^{2+}, and Mn^{2+} correlate with their relative tendencies to be acidic?
10. An individual measured the pH of a water sample as 11.2 and reported it to be "highly alkaline." Is that statement necessarily true?
11. Match the following pertaining to properties of water (left) and their effects and significance (right):

A. Highest dielectric constant of any common liquid	1. Stabilization of temperatures of organisms and geographical regions
B. Higher surface tension than any other liquid	2. Controlling factor in physiology; governs drop and surface phenomena
C. Maximum density as a liquid	3. High solubility of ionic substances and their ionization in aqueous solution
D. Higher heat capacity than any liquid other than ammonia	4. Ice floats

12. How does the temperature-density relationship of water influence the presence of oxidized and reduced species in a body of water?
13. What is a particularly unique aspect of oceanographic chemistry?
14. Explain with appropriate chemical reactions how the fixation of inorganic carbon by algal photosyntheis in water can result in the eventual precipitation of $CaCO_3$.
15. The chemical species that is the predominant contributor to water alkalinity is _____ and the predominant contributor to water hardness is _____.
16. In what sense is pH an *intensity* factor, and alkalinity a *capacity* factor? How do the comparative pHs and alkalinities of 1.00×10^{-3} M NaOH and 0.100 M HCO_3^- illustrate this point?
17. Illustrate with a chemical reaction how the addition of $Al(H_2O)_6^{3+}$ might reduce alkalinity in water.
18. Explain what the chemical formula Mg^{2+}, used to represent magnesium ion dissolved in water, really means.
19. Explain what the following chemical formulas have to do with speciation of metals dissolved in water: $Fe(H_2O)_6^{3+}$, $Fe(CN)_6^{3-}$, $Pb(C_2H_5)_4$, where C_2H_5 is an ethyl group bound to lead through a carbon atom.
20. What does the reaction below show about water chemistry, hardness, and alkalinity? How is microbial degradation of organic matter tied in with the phenomenon illustrated?

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$CaCO_3(s) + CO_2(aq) + H_2O \leftarrow\rightarrow Ca^{2+} + 2HCO_3^-$

21. Explain how the reaction below illustrates a detrimental aspect of water hardness.

 $2C_{17}H_{33}COO^-Na^+ + Ca^{2+} \rightarrow Ca(C_{17}H_{33}CO_2)_2(s) + 2Na^+$

22. Explain what the two reactions below show about oxidation-reduction phenomena in water. How are they tied in with pE in water? How is pE conceptually defined?

 $2H_2O + 2e^- \leftarrow\rightarrow H_2(g) + 2OH^-$

 $2H_2O \leftarrow\rightarrow O_2(g) + 4H^+ + 4e^-$

23. Define ligand, complex, and chelating agent. Why is a chelate often so stable? How are "electron pairs" involved in complexation and chelation? What is a unidentate ligand?

24. Explain in what sense the species $Fe(H_2O)_6^{2+}$ is a complex ion.

25. Explain some of the major environmental implications of complexation and chelation. What is the particular environmental harm that might come from codisposal of a toxic heavy metal salt and a chelating compound?

26. In what sense does an organometallic compound differ from a complex compound?

27. What are the three classes of humic substances? What is the source of humic substances? What are their chelating properties?

28. What are some of the unique characteristics of colloidal particles that make them so important in water? What is the approximate size of colloidal particles?

29. How are sediments formed? Discuss the significance of sediments in aquatic chemistry.

30. Define the following terms as applied to aquatic organisms and give an example of each: Autotrophic organisms, heterotrophic organisms, producers, decomposers, aerobic bacteria, anaerobic bacteria.

31. List and discuss the reasons that microorganisms are of particular importance in water.

32. Give the name and significance of each of the following compounds or microbially-mediated reactions involving sulfur: (1) $SO_4^{2-} + 2\{CH_2O\} + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O$, (2) $2H_2S + 4O_2 \rightarrow 4H^+ + 2SO_4^{2-}$, (3) CH_3SH.

33. What are the important implications for environmental chemistry of the fact that aquatic bacteria are extremely small and may reproduce very rapidly?

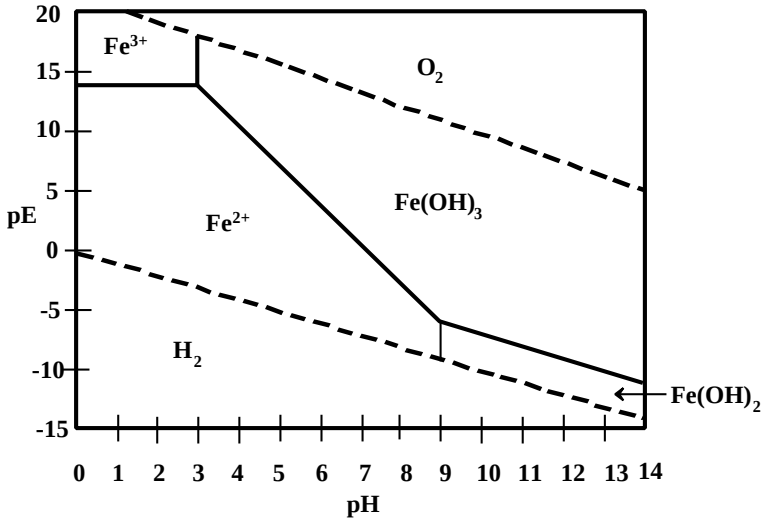
34. Define algae and fungi. Give a simplified biochemical reaction characteristic of algae and one characteristic of fungi. In what sense are fungi and algae "opposites"? Why is *cellulase* particularly important in environmental chemical processes?

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35. Define each of the following applied to aquatic bacteria: Cell wall, slime layer, cell membrane, flagella, cytoplasm, nuclear body, inclusions.

36. Offer plausible explanations for the four regions shown in a bacterial growth curve. What are the special implications of the log region?

37. In the pE-pH diagram below, suppose that the upper dashed line represents equilibrium of the system shown with atmospheric oxygen and that the lower dashed line represents equilibrium with an anaerobic system, such as in the sediment of a body of water. That being the case, use arrows and reactions to explain the following in a system in which some iron is available: (1) Acid mine water typically contains dissolved iron in equilibrium with air. Which region on the diagram might represent acid mine water? (2) What is observed as the pH of iron-containing acid mine water is raised by dilution or exposure to base? (3) Explain the presence of soluble iron in anaerobic groundwater at pH 7. (4) Explain what might happen, and why a precipitate might be observed, as acid mine water is raised to the surface and exposed to air.



38. Explain the plot showing the effect of increasing substrate concentration on enzyme activity.

39. Explain the plot showing the effect of temperature on bacterial enzyme activity and growth. Why is it unsymmetrical?

39. Explain the significance of each of the following in the carbon cycle: Photosynthesis, the biochemical reaction $\{CH_2O\} + O_2(g) \rightarrow CO_2 + H_2O$, methane production, β–oxidation.

40. What is an important characteristic of *Thiobacillus thiooxidans* that make it responsible for adverse conditions that it may, itself, create through its metabolic action on species in water? Explain.

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41. Give the name and significance of each of the following microbially-mediated reactions involving nitrogen: (1) $3\{CH_2O\} + 2N_2 + 3H_2O + 4H^+ \rightarrow 3CO_2 + 4NH_4^+$, (2) $2O_2 + NH_4^+ \rightarrow NO_3^- + 2H^+ + H_2O$, (3) $2NO_3^- + \{CH_2O\} \rightarrow 2NO_2^- + H_2O + CO_2$, (4) $2NO_2^- + 3\{CH_2O\} + 4H^+ \rightarrow 2NH_4^+ + 3CO_2 + H_2O$, (5) $4NO_3^- + 5\{CH_2O\} + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O$

42. Give two reasons why biodegradation of phosphorus compounds in the environment is important.

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Manahan, Stanley E. "WATER POLLUTION"
Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

12 WATER POLLUTION

12.1 NATURE AND TYPES OF WATER POLLUTANTS

Throughout history, the quality of drinking water has been a factor in determining human welfare. Fecal pollution of drinking water has frequently caused waterborne diseases that have decimated the populations of whole cities. Unwholesome water polluted by natural sources has caused great hardship for people forced to drink it or use it for irrigation.

Although there are still occasional epidemics of bacterial and viral diseases caused by infectious agents carried in drinking water, waterborne diseases have in general been well controlled, and drinking water in technologically advanced countries is now remarkably free of the disease-causing agents that were very common water contaminants only a few decades earlier.

Currently, waterborne toxic chemicals pose the greatest threat to the safety of water supplies in industrialized nations. This is particularly true of groundwater in the U.S., which exceeds in volume the flow of all U.S. rivers, lakes, and streams. In some areas, the quality of groundwater is subject to a number of chemical threats. There are many possible sources of chemical contamination. These include wastes from industrial chemical production, metal-plating operations, and pesticide runoff from agricultural lands. Some specific pollutants include industrial chemicals such as chlorinated hydrocarbons; heavy metals, including cadmium, lead, and mercury; saline water; bacteria, particularly coliforms; and general municipal and industrial wastes.

Since World War II, there has been a tremendous growth in the manufacture and use of synthetic chemicals. Many of the chemicals have contaminated water supplies. Two examples are insecticide and herbicide runoff from agricultural land, and industrial discharge into surface waters. Also, there is a threat to groundwater from waste chemical dumps and landfills, storage lagoons, treating ponds, and other facilities. These threats are discussed in more detail in Chapter 21.

It is clear that water pollution should be a concern of every citizen. Understanding the sources, interactions, and effects of water pollutants is essential for

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controlling pollutants in an environmentally safe and economically acceptable manner. Above all, an understanding of water pollution and its control depends upon a basic knowledge of aquatic environmental chemistry. That is why this text covers the principles of aquatic chemistry prior to discussing pollution. Water pollution can be studied much more effectively with a sound background in the fundamental properties of water, aquatic microbial reactions, sediment-water interactions, and other factors involved with the reactions, transport, and effects of these pollutants.

Water pollutants can be divided among some general categories, as summarized in Table 12.1. Most of these categories of pollutants, and several subcategories, are discussed in this chapter. An enormous amount of material is published on this subject each year, and it is impossible to cover it all in one chapter. To be up to date on this subject, the reader may want to survey journals and books dealing with water pollution, such as those listed in the Supplementary References section at the end of this chapter.

Table 12.1 General Types of Water Pollutants

Class of pollutant	Significance
Trace Elements	Health, aquatic biota, toxicity
Heavy metals	Health, aquatic biota, toxicity
Organically bound metals	Metal transport
Radionuclides	Toxicity
Inorganic pollutants	Toxicity, aquatic biota
Asbestos	Human health
Algal nutrients	Eutrophication
Acidity, alkalinity, salinity (in excess)	Water quality, aquatic life
Trace organic pollutants	Toxicity
Polychlorinated biphenyls	Possible biological effects
Pesticides	Toxicity, aquatic biota, wildlife
Petroleum wastes	Effect on wildlife, esthetics
Sewage, human and animal wastes	Water quality, oxygen levels
Biochemical oxygen demand	Water quality, oxygen levels
Pathogens	Health effects
Detergents	Eutrophication, wildlife, esthetics
Chemical carcinogens	Incidence of cancer
Sediments	Water quality, aquatic biota, wildlife
Taste, odor, and color	Esthetics

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12.2 ELEMENTAL POLLUTANTS

Trace element is a term that refers to those elements that occur at very low levels of a few parts per million or less in a given system. The term **trace substance** is a more general one applied to both elements and chemical compounds.

Table 12.2 summarizes the more important trace elements encountered in natural waters. Some of these are recognized as nutrients required for animal and plant life, including some that are essential at low levels but toxic at higher levels. This is typical behavior for many substances in the aquatic environment, a point that must be

Table 12.2 Important Trace Elements in Natural Waters

Element	Sources	Effects and Significance
Arsenic	Mining byproduct, chemical waste	Toxic[1], possibly carcinogenic
Beryllium	Coal, industrial wastes	Toxic
Boron	Coal, detergents, wastes	Toxic
Chromium	Metal plating	Essential as Cr(III), toxic as Cr(VI)
Copper	Metal plating, mining, industrial waste	Essential trace element, toxic to plants and algae at higher levels
Fluorine (F^-)	Natural geological sources, wastes, water additive	Prevents tooth decay at around 1 mg/L, toxic at higher levels
Iodine (I^-)	Industrial wastes, natural brines, seawater intrusion	Prevents goiter
Iron	Industrial wastes, corrosion, acid mine water, microbial action	Essential nutrient, damages fixtures by staining
Lead	Industrial waste, mining, fuels	Toxic, harmful to wildlife
Manganese	Industrial wastes, acid mine water, microbial action	Toxic to plants, damages fixtures by staining
Mercury	Industrial waste, mining, coal	Toxic, mobilized as methyl mercury compounds by anaerobic bacteria
Molybdenum	Industrial wastes, natural sources	Essential to plants, toxic to animals
Selenium	Natural sources, coal	Essential at lower levels, toxic at higher levels
Zinc	Industrial waste, metal plating, plumbing	Essential element, toxic to plants at higher levels

[1] Toxicities of these elements are discussed in Chapter 23.

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kept in mind in judging whether a particular element is beneficial or detrimental. Some of these elements, such as lead or mercury, have such toxicological and environmental significance that they are discussed in detail in separate sections.

Some of the **heavy metals** are among the most harmful of the elemental pollutants and are of particular concern because of their toxicities to humans. These elements are, in general, the transition metals, and some of the representative elements, such as lead and tin, in the lower right-hand corner of the periodic table. Heavy metals include essential elements like iron as well as toxic metals like cadmium and mercury. Most of them have a tremendous affinity for sulfur, and disrupt enzyme function by forming bonds with sulfur groups in enzymes. Protein carboxylic acid ($-CO_2H$) and amino ($-NH_2$) groups are also chemically bound by heavy metals. Cadmium, copper, lead, and mercury ions bind to cell membranes, hindering transport processes through the cell wall. Heavy metals may also precipitate phosphate biocompounds or catalyze their decomposition. The biochemical effects of metals are discussed in Chapter 23.

Some of the **metalloids**, elements on the borderline between metals and nonmetals, are significant water pollutants. Arsenic, selenium, and antimony are of particular interest.

Inorganic chemicals manufacture has the potential to contaminate water with trace elements. Among the industries regulated for potential trace element pollution of water are those producing chlor-alkali, hydrofluoric acid, sodium dichromate (sulfate process and chloride ilmenite process), aluminum fluoride, chrome pigments, copper sulfate, nickel sulfate, sodium bisulfate, sodium hydrosulfate, sodium bisulfite, titanium dioxide, and hydrogen cyanide.

12.3 HEAVY METALS

Cadmium

Pollutant **cadmium** in water may arise from industrial discharges and mining wastes. Cadmium is widely used in metal plating. Chemically, cadmium is very similar to zinc, and these two metals frequently undergo geochemical processes together. Both metals are found in water in the +2 oxidation state.

The effects of acute cadmium poisoning in humans are very serious. Among them are high blood pressure, kidney damage, destruction of testicular tissue, and destruction of red blood cells. It is believed that much of the physiological action of cadmium arises from its chemical similarity to zinc. Specifically, cadmium may replace zinc in some enzymes, thereby altering the stereostructure of the enzyme and impairing its catalytic activity. Disease symptoms ultimately result.

Lead

Inorganic **lead** arising from a number of industrial and mining sources occurs in water in the +2 oxidation state. Lead from leaded gasoline used to be a major source of atmospheric and terrestrial lead, much of which eventually entered natural water systems. In addition to pollutant sources, lead-bearing limestone and galena (PbS) contribute lead to natural waters in some locations.

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Despite greatly increased total use of lead by industry, evidence from hair samples and other sources indicates that body burdens of this toxic metal have decreased during recent decades. This may be in part the result of less lead used in plumbing and other products that come in contact with food or drink.

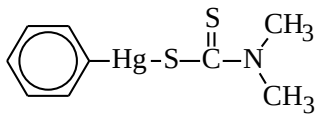
Acute lead poisoning in humans may cause severe dysfunction of the kidney, reproductive system, liver, brain, and central nervous system leading to sickness or death. Lead poisoning from environmental exposure is thought to have caused mental retardation in many children. Mild lead poisoning causes anemia. The victim may have headaches and sore muscles, and may feel generally fatigued and irritable.

Except in isolated cases, lead is probably not a major problem in drinking water, although the potential exists in cases where old lead pipe is still in use. Lead used to be a constituent of solder and some pipe-joint formulations, so that household water does have some contact with lead. Water that has stood in household plumbing for some time may accumulate significant levels of lead (along with zinc, cadmium, and copper) and should be drained for a while before use.

Mercury

Because of its toxicity, mobilization as methylated forms by anaerobic bacteria, and other pollution factors, **mercury** generates a great deal of concern as a heavy-metal pollutant. Mercury is found as a trace component of many minerals, with continental rocks containing an average of around 80 parts per billion, or slightly less, of this element. Cinnabar, red mercuric sulfide, is the chief commercial mercury ore. Fossil fuel coal and lignite contain mercury, often at levels of 100 parts per billion or even higher, a matter of some concern with increased use of these fuels for energy resources.

Metallic mercury is used as an electrode in the electrolytic generation of chlorine gas, in laboratory vacuum apparatus, and in other applications. Significant quantities of inorganic mercury(I) and mercury(II) compounds are used annually. Organic mercury compounds used to be widely applied as pesticides, particularly fungicides. These mercury compounds include aryl mercurials such as phenyl mercuric dimethyldithiocarbamate



(formerly used in paper mills as a slimicide and as a mold retardant for paper), and alkyl-mercurials such as ethylmercuric chloride, C_2H_5HgCl, which was used as a seed fungicide. Because of their resistance to degradation and their mobility, the alkyl mercury compounds are generally considered to be more of an environmental threat than either the aryl or inorganic compounds.

Mercury enters the environment from a large number of miscellaneous sources related to human use of the element. These include discarded laboratory chemicals, batteries, broken thermometers, amalgam tooth fillings, and formerly lawn fungicides and pharmaceutical products. Taken individually, each of these sources may not contribute much of the toxic metal, but the total effect can be substantial. Sewage

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effluent sometimes contains up to 10 times the level of mercury found in typical natural waters.

The toxicity of mercury was tragically illustrated in the Minamata Bay area of Japan during the period 1953–1960. A total of 111 cases of mercury poisoning and 43 deaths were reported among people who had consumed seafood from the bay that had been contaminated with mercury waste from a chemical plant that drained into Minamata Bay. Congenital defects were observed in 19 babies whose mothers had consumed seafood contaminated with mercury. The level of metal in the contaminated seafood was 5–20 parts per million.

Among the toxicological effects of mercury are neurological damage, including irritability, paralysis, blindness, or insanity; chromosome breakage; and birth defects. The milder symptoms of mercury poisoning such as depression and irritability have a psychopathological character. Because of the resemblance of these symptoms to common human behavior, mild mercury poisoning may escape detection. Some forms of mercury are relatively nontoxic and were formerly used as medicines, for example, in the treatment of syphilis. Other forms of mercury, such as soluble Hg(II) salts and methylmercury compounds, are highly toxic.

Because there are few major natural sources of mercury, and since most inorganic compounds of this element are relatively insoluble, it was assumed for some time that mercury was not a serious water pollutant. However, in 1970, alarming mercury levels were discovered in fish in Lake Saint Clair, which is located between Michigan and Ontario, Canada. A subsequent survey by the U.S. Federal Water Quality Administration revealed a number of other waters contaminated with mercury. It was found that several chemical plants, particularly caustic chemical manufacturing operations, were each releasing up to 14 or more kilograms of mercury in wastewaters each day.

The unexpectedly high concentrations of mercury found in water and in fish tissues result from the formation of soluble monomethylmercury ion, CH_3Hg^+, and volatile dimethylmercury, $(CH_3)_2Hg$, by anaerobic bacteria in sediments. Mercury from these compounds becomes concentrated in fish lipid (fat) tissue and the concentration factor from water to fish may exceed 10^3. The methylating agent by which inorganic mercury is converted to methylmercury compounds is methylcobalamin, a vitamin B_{12} analog:

$$HgCl_2 \xrightarrow{\text{Methylcobalamin}} CH_3HgCl + Cl^- \qquad (12.3.1)$$

It is believed that the bacteria that synthesize methane produce methylcobalamin as an intermediate in the synthesis. Thus, waters and sediments in which anaerobic decay is occurring provide the conditions under which methylmercury production occurs. In neutral or alkaline waters, the formation of dimethylmercury, $(CH_3)_2Hg$, is favored. This volatile compound can escape to the atmosphere.

12.4 METALLOIDS

The most significant water pollutant metalloid element is arsenic, a toxic element that has been the chemical villain of more than a few murder plots. Acute arsenic

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poisoning can result from the ingestion of more than about 100 mg of the element. Chronic poisoning occurs with the ingestion of small amounts of arsenic over a long period of time. There is some evidence that this element is also carcinogenic.

Arsenic occurs in the Earth's crust at an average level of 2–5 ppm. The combustion of fossil fuels, particularly coal, introduces large quantities of arsenic into the environment, much of it reaching natural waters. Arsenic occurs with phosphate minerals and enters into the environment along with some phosphorus compounds. Some formerly used pesticides, particularly those from before World War II, contain highly toxic arsenic compounds. The most common of these are lead arsenate, $Pb_3(AsO_4)_2$; sodium arsenite, Na_3AsO_3; and Paris Green, $Cu_3(AsO_3)_2$. Another major source of arsenic is mine tailings. Arsenic produced as a by-product of copper, gold, and lead refining exceeds the commercial demand for arsenic, and it accumulates as waste material.

Like mercury, arsenic can be converted by bacteria to more mobile and toxic methyl derivatives according to the following reactions:

$$H_3AsO_4 + 2H^+ + 2e^- \rightarrow H_3AsO_3 + H_2O \quad (12.4.1)$$

$$H_3AsO_3 \xrightarrow{\text{Methylcobalamin}} \underset{\text{Methylarsinic acid}}{CH_3AsO(OH)_2} \quad (12.4.2)$$

$$CH_3AsO(OH)_2 \xrightarrow{\text{Methylcobalamin}} \underset{\text{(Dimethylarsinic acid)}}{(CH_3)_2AsO(OH)} \quad (12.4.3)$$

$$(CH_3)_2AsO(OH) + 4H^+ + 4e^- \rightarrow (CH_3)_2AsH + 2H_2O \quad (12.4.4)$$

12.5 ORGANICALLY BOUND METALS AND METALLOIDS

An appreciation of the strong influence of complexation and chelation on heavy metals' behavior in natural waters and wastewaters can be gained by reading Section 11.9, which deals with that subject. Methylmercury formation is also discussed in Section 11.9. Both topics involve the combination of metals and organic entities in water. The interaction of metals with organic compounds is of utmost importance in determining the role played by the metal in an aquatic system.

There are two major types of metal-organic interactions to be considered in an aquatic system. The first of these is complexation, usually chelation when organic ligands are involved. A reasonable definition of complexation by organics applicable to natural water and wastewater systems is a system in which a species is present that reversibly dissociates to a metal ion and an organic complexing species as a function of hydrogen ion concentration:

$$ML + 2H^+ \leftrightarrow M^{2+} + H_2L \quad (12.5.1)$$

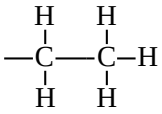
In this equation, M^{2+} is a metal ion and H_2L is the acidic form of a complexing—frequently chelating—ligand, L^{2-}, illustrated here as a compound that has two ionizable hydrogens.

Organometallic compounds, on the other hand, contain metals bound to organic entities by way of a carbon atom and do not dissociate reversibly at lower pH or

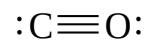
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greater dilution. Furthermore, the organic component, and sometimes the particular oxidation state of the metal involved, may not be stable apart from the organometallic compound. A simple way to classify organometallic compounds for the purpose of discussing their toxicology is the following:

1. Those in which the organic group is an alkyl group such as ethyl in tetraethyllead, $Pb(C_2H_5)_4$:

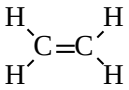


2. **Carbonyls**, some of which are quite volatile and toxic, having carbon monoxide bonded to metals:



(In the preceding Lewis formula of CO each dash, –, represents a pair of bonding electrons, and each pair of dots, **:**, represents an unshared pair of electrons.)

3. Those in which the organic group is a π electron donor, such as ethylene or benzene.



Ethylene



Benzene

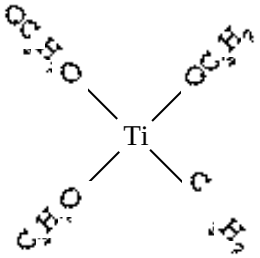
Combinations exist of the three general types of compounds outlined above, the most prominent of which are arene carbonyl species in which a metal atom is bonded to both an aryl entity such as benzene and to several carbon monoxide molecules.

A large number of compounds exist that have at least one bond between the metal and a C atom on an organic group, as well as other covalent or ionic bonds between the metal and atoms other than carbon. Because they have at least one metal-carbon bond, as well as properties, uses, and toxicological effects typical of organometallic compounds, it is useful to consider such compounds along with organometallic compounds. Examples are monomethylmercury chloride, CH_3HgCl, in which the organometallic CH_3Hg^+ ion is ionically bonded to the chloride anion. Another example is phenyldichloroarsine, $C_6H_5AsCl_2$, in which a phenyl group is covalently bonded to arsenic through an As-C bond, and two Cl atoms are also covalently bonded to arsenic.

A number of compounds exist that consist of organic groups bonded to a metal atom through atoms other than carbon. Although they do not meet the strict definition thereof, such compounds can be classified as organometallics for the discussion of their toxicology and aspects of their chemistry. An example of such a compound is isopropyl titanate, $Ti(i\text{-}OC_3H_7)_4$, also called titanium isopropylate (next page), a colorless liquid melting at 14.8˚C and boiling at 104˚C. Its behavior is more that of an organometallic compound than that of an inorganic compound, and, by virtue of its titanium content, it is not properly classified as an organic compound.

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The term “organometal” is sometimes applied to such a compound, which for environmental considerations can be regarded as an organometallic compound.



Titanium isopropylate

The interaction of trace metals with organic compounds in natural waters is too vast an area to cover in detail in this chapter; however, it can be noted that metal-organic interactions may involve organic species of both pollutant (such as EDTA) and natural (such as fulvic acids) origin. These interactions are influenced by, and sometimes play a role in, redox equilibria; formation and dissolution of precipitates; colloid formation and stability; acid-base reactions; and microorganism-mediated reactions in water. Metal-organic interactions may increase or decrease the toxicity of metals in aquatic ecosystems, and they have a strong influence on the growth of algae in water.

Organotin Compounds

Of all the metals, tin has the greatest number of organometallic compounds in commercial use, with global production on the order of 40,000 metric tons per year. In addition to synthetic organotin compounds, methylated tin species can be produced biologically in the environment. Figure 12.1 gives some examples of the many known organotin compounds.

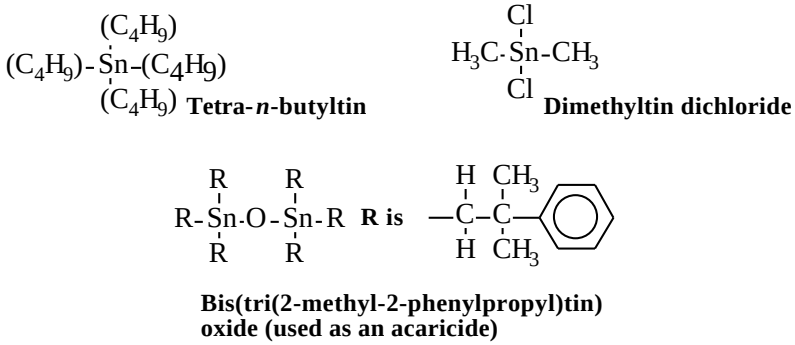


figure 12.1 Examples of organotin compounds.

Major industrial uses of organotin compounds include applications of tin compounds in fungicides, acaricides, disinfectants, antifouling paints, stabilizers to lessen the effects of heat and light in PVC plastics, catalysts, and precursors for the formation of films of SnO_2 on glass. Tributyl tin chloride and related tributyl tin (TBT) compounds have bactericidal, fungicidal, and insecticidal properties and are

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of particular environmental significance because of their use as industrial biocides. In addition to tributyl tin chloride, other tributyl tin compounds used as biocides include the hydroxide, the naphthenate, bis(tributyltin) oxide, and tris(tributyl-stannyl) phosphate. TBT has been widely used in boat and ship hull coatings to prevent the growth of fouling organisms. Other applications include preservation of wood, leather, paper, and textiles. Antifungal TBT compounds have been used as slimicides in cooling tower water.

Obviously, the many applications of organotin compounds for a variety of uses pose a significant potential for environmental pollution. Because of their applications near or in contact with bodies of water, organotin compounds are potentially significant water pollutants and have been linked to endocrine disruption in shellfish, oysters, and snails. Because of such concerns, several countries, including the U.S., England, and France, prohibited TBT application on vessels smaller than 25 meters in length during the 1980s. In response to concerns over water pollution, in 1998 the International Maritime Organization agreed to ban organotin antifouling paints on all ships by 2003.

12.6 INORGANIC SPECIES

Some important inorganic water pollutants were mentioned in Sections 12.2–12.4 as part of the discussion of pollutant trace elements. Inorganic pollutants that contribute acidity, alkalinity, or salinity to water are considered separately in this chapter. Still another class is that of algal nutrients. This leaves unclassified, however, some important inorganic pollutant species, of which cyanide ion, CN^-, is probably the most important. Others include ammonia, carbon dioxide, hydrogen sulfide, nitrite, and sulfite.

Cyanide

Cyanide, a deadly poisonous substance, exists in water as HCN, a weak acid, K_a of 6×10^{-10}. The cyanide ion has a strong affinity for many metal ions, forming relatively less-toxic ferrocyanide, $Fe(CN)_6^{4-}$, with iron(II), for example. Volatile HCN is very toxic and has been used in gas chamber executions in the U.S.

Cyanide is widely used in industry, especially for metal cleaning and electroplating. It is also one of the main gas and coke scrubber effluent pollutants from gas works and coke ovens. Cyanide is widely used in certain mineral-processing operations. In August of 1995, approximately 2.7 billion liters of cyanide-contaminated water mixed with red clay from mine tailings spilled into the Essequibo River from a breached dam at a gold mining operation in the South American country of Guyana. The water contained cyanide at a level of approximately 25 parts per million, which killed all the fish in the small Omai Creek leading from the breached dam to the Essequibo River. No human fatalities or confirmed health effects were reported, however.

Ammonia and Other Inorganic Pollutants

Excessive levels of ammoniacal nitrogen cause water-quality problems. **Ammonia** is the initial product of the decay of nitrogenous organic wastes, and its presence frequently indicates the presence of such wastes. It is a normal constituent

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of low-pE groundwaters and is sometimes added to drinking water, where it reacts with chlorine to provide residual chlorine (see Section 13.11). Since the pK_a of ammonium ion, NH_4^+, is 9.26, most ammonia in water is present as NH_4^+ rather than as NH_3.

Hydrogen sulfide, H_2S, is a product of the anaerobic decay of organic matter containing sulfur. It is also produced in the anaerobic reduction of sulfate by microorganisms (see Chapter 11, Section 11.13) and is evolved as a gaseous pollutant from geothermal waters. Wastes from chemical plants, paper mills, textile mills, and tanneries may also contain H_2S. Its presence is easily detected by its characteristic rotten-egg odor. In water, H_2S is a weak diprotic acid with pK_{a1} of 6.99 and pK_{a2} of 12.92; S^{2-} is not present in normal natural waters. The sulfide ion has tremendous affinity for many heavy metals, and precipitation of metallic sulfides often accompanies production of H_2S.

Free **carbon dioxide**, CO_2, is frequently present in water at high levels due to decay of organic matter. It is also added to softened water during water treatment as part of a recarbonation process (see Chapter 13, Section 13.7). Excessive carbon dioxide levels may make water more corrosive, therefore, damaging to water distribution systems, and may be harmful to aquatic life.

Nitrite ion, NO_2^-, occurs in water as an intermediate oxidation state of nitrogen over a relatively narrow pE range. Nitrite is added to some industrial process water as a corrosion inhibitor. However, it rarely occurs in drinking water at levels over 0.1 mg/L.

Sulfite ion, SO_3^{2-}, is found in some industrial wastewaters. Sodium sulfite is commonly added to boiler feedwaters as an oxygen scavenger where it reacts to remove potentially corrosive dissolved molecular oxygen from the water:

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-} \quad (12.6.1)$$

Since pK_{a1} of sulfurous acid is 1.76 and pK_{a2} is 7.20, sulfite exists as either HSO_3^- or SO_3^{2-} in natural waters, depending upon pH. It may be noted that hydrazine, N_2H_4, also functions as an oxygen scavenger:

$$N_2H_4 + O_2 \rightarrow 2H_2O + N_2(g) \quad (12.6.2)$$

Asbestos in Water

The toxicity of inhaled asbestos is well established. The fibers scar lung tissue and cancer eventually develops, often 20 or 30 years after exposure. It is not known for sure whether asbestos is toxic in drinking water. This has been a matter of considerable concern because of the dumping of taconite (iron ore tailings) containing asbestos-like fibers into Lake Superior. The fibers have been found in drinking waters of cities around the lake. After having dumped the tailings into Lake Superior since 1952, the Reserve Mining Company at Silver Bay on Lake Superior solved the problem in 1980 by constructing a 6-square-mile containment basin inland from the lake. This $370-million facility keeps the taconite tailings covered with a 3-meter layer of water to prevent escape of fiber dust.

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12.7 ALGAL NUTRIENTS AND EUTROPHICATION

The term **eutrophication**, derived from the Greek word meaning "well-nourished," describes a condition of lakes or reservoirs involving excess algal growth. Although some algal productivity is necessary to support the food chain in an aquatic ecosystem, excess growth under eutrophic conditions may eventually lead to severe deterioration of the body of water. The first step in eutrophication of a body of water is an input of plant nutrients (Table 12.3) from watershed runoff or sewage. The nutrient-rich body of water then produces a great deal of plant biomass by photosynthesis, along with a smaller amount of animal biomass. Dead biomass accumulates in the bottom of the lake, where it undergoes partial mineralization, recycling nutrient carbon dioxide, phosphorus, nitrogen, and potassium. If the lake is not too deep, bottom-rooted plants begin to grow, accelerating the accumulation of solid material in the basin. Eventually, a marsh is formed that finally fills in to produce a meadow or forest.

Eutrophication is often a natural phenomenon; for instance, it is basically responsible for the formation of huge deposits of coal and peat. However, human activity can greatly accelerate the process. To understand why this is so, refer to Table 12.3, which shows the chemical elements needed for plant growth. Most of these are present at levels more than sufficient to support plant life in the average lake or reservoir. Hydrogen and oxygen come from the water itself. Carbon is provided by CO_2 from the atmosphere or from decaying vegetation. Sulfate, magnes-

Table 12.3 Essential Plant Nutrients: Sources and Functions

Nutrient	Source	Function
Macronutrients		
Carbon (CO_2)	Atmosphere, decay	Biomass constituent
Hydrogen	Water	Biomass constituent
Oxygen	Water	Biomass constituent
Nitrogen (NO_3^-)	Decay, pollutants, atmosphere (from nitrogen-fixing organisms)	Protein constituent
Phosphorus (phosphate)	Decay, minerals, pollutants	DNA/RNA constituent
Potassium	Minerals, pollutants	Metabolic function
Sulfur (sulfate)	Minerals	Proteins, enzymes
Magnesium	Minerals	Metabolic function
Calcium	Minerals	Metabolic function
Micronutrients		
B, Cl, Co, Cu, Fe, Mo, Mn, Na, Si, V, Zn	Minerals, pollutants	Metabolic function and/or constituent of enzymes

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ium, and calcium are normally present in abundance from mineral strata in contact with the water. The micronutrients are required at only very low levels (for example, approximately 40 ppb for copper). Therefore, the nutrients most likely to be limiting are the "fertilizer" elements: nitrogen, phosphorus, and potassium. These are all present in sewage and are, of course, found in runoff from heavily fertilized fields. They are also constituents of various kinds of industrial wastes. Each of these elements can also come from natural sources—phosphorus and potassium from mineral formations, and nitrogen fixed by bacteria, cyanobacteria, or discharge of lightning in the atmosphere.

In most cases, the single plant nutrient most likely to be limiting is phosphorus, and it is generally named as the culprit in excessive eutrophication. Household detergents are a common source of phosphate in wastewater, and eutrophication control has concentrated upon eliminating phosphates from detergents, removing phosphate at the sewage treatment plant, and preventing phosphate-laden sewage effluents (treated or untreated) from entering bodies of water.

In some cases, nitrogen or even carbon may be limiting nutrients. This is particularly true of nitrogen in seawater.

The whole eutrophication picture is a complex one, and continued research is needed to solve the problem. It is indeed ironic that in a food-poor world, nutrient-rich wastes from overfertilized fields or from sewage are causing excessive plant growth in many lakes and reservoirs. This illustrates a point that, in many cases, pollutants are resources (in this case, plant nutrients) gone to waste.

12.8 ACIDITY, ALKALINITY, AND SALINITY

Aquatic biota are sensitive to extremes of pH. Largely because of osmotic effects, they cannot live in a medium having a salinity to which they are not adapted. Thus, a freshwater fish soon succumbs in the ocean, and sea fish normally cannot live in fresh water. Excess salinity soon kills plants not adapted to it. There are, of course, ranges in salinity and pH in which organisms live. As shown in Figure 12.2, these ranges frequently can be represented by a reasonably symmetrical curve, along the fringes of which an organism may live without really thriving.

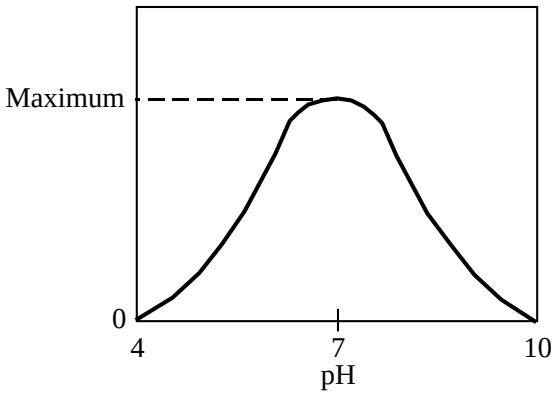


Figure 12.2 A generalized plot of the growth of an aquatic organism as a function of pH.

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The most common source of **pollutant acid** in water is acid mine drainage. Acid mine water results from the presence of sulfuric acid produced by the oxidation of pyrite, FeS_2. Microorganisms are closely involved in the overall process, which consists of several reactions. The first of these reactions is the bacterially mediated oxidation of pyrite:

$$2FeS_2(s) + 2H_2O + 7O_2 \rightarrow 4H^+ + 4SO_4^{2-} + 2Fe^{2+} \quad (12.8.1)$$

The next step is the oxidation of iron(II) ion to iron(III) ion,

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (12.8.2)$$

a process that occurs very slowly by purely chemical processes at the low pH values found in acid mine waters, but is accelerated by the action of bacteria. Below pH 3.5, the iron oxidation is catalyzed by the iron bacterium *Thiobacillus ferrooxidans*, and in the pH range 3.5-4.5 it may be catalyzed by a variety of *Metallogenium*, a filamentous iron bacterium. Other bacteria that may be involved in acid mine water formation are *Thiobacillus thiooxidans* and *Ferrobacillus ferrooxidans*. The Fe^{3+} ion further dissolves pyrite,

$$FeS_2(s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (12.8.3)$$

which in conjunction with Reaction 12.8.2 constitutes a cycle for the dissolution of pyrite. $Fe(H_2O)_6^{3+}$ is an acidic ion and at pH values much above 3, the iron(III) precipitates as the hydrated iron(III) oxide:

$$Fe^{3+} + 3H_2O \leftarrow\rightarrow Fe(OH)_3(s) + 3H^+ \quad (12.8.4)$$

The beds of streams afflicted with acid mine drainage often are covered with "yellowboy," an unsightly deposit of amorphous, semigelatinous $Fe(OH)_3$.

The most damaging component of acid mine water is sulfuric acid. It is directly toxic and has other undesirable effects. The values of pH encountered in acid-polluted water may fall below 3, a condition deadly to most forms of aquatic life except the culprit bacteria mediating the pyrite and iron(II) oxidation, which thrive under very low pH conditions. Industrial wastes frequently have the potential to contribute strong acid to water. Sulfuric acid produced by the air oxidation of pollutant sulfur dioxide (see Chapter 15) enters natural waters as acidic rainfall. In cases where the water does not have contact with a basic mineral, such as limestone, the water pH may become dangerously low. This condition occurs in some Canadian lakes, for example.

Excess **alkalinity**, and frequently accompanying high pH, generally are not introduced directly into water from anthropogenic sources. However, in many geographic areas, the soil and mineral strata are alkaline and impart a high alkalinity to water. Human activity can aggravate the situation—for example, by exposure of alkaline overburden from strip mining to surface water or groundwater. Excess alkalinity in water is manifested by a characteristic fringe of white salts at the edges of a body of water or on the banks of a stream.

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Water **salinity** may be increased by a number of human activities. Water passing through a municipal water system inevitably picks up salt from a number of processes; for example, recharging water softeners with sodium chloride is a major contributor to salinity in municipal wastewater. Salts can leach from spoil piles. One of the major environmental constraints on the production of shale oil, for example, is the high percentage of leachable sodium sulfate in piles of spent shale. Careful control of these wastes is necessary to prevent further saline pollution of water in areas where salinity is already a problem. Irrigation adds a great deal of salt to water, a phenomenon responsible for the Salton Sea in California, and is a source of conflict between the United States and Mexico over saline contamination of the Rio Grande and Colorado rivers. Irrigation and intensive agricultural production have caused saline seeps in some of the Western states. These occur when water seeps into a slight depression in tilled, sometimes irrigated, fertilized land, carrying salts (particularly sodium, magnesium, and calcium sulfates) along with it. The water evaporates in the dry summer heat, leaving behind a salt-laden area that no longer supports much plant growth. With time, these areas spread, destroying the productivity of crop land.

12.9 OXYGEN, OXIDANTS, AND REDUCTANTS

Oxygen is a vitally important species in water (see Chapter 11). In water, oxygen is consumed rapidly by the oxidation of organic matter, $\{CH_2O\}$:

$$\{CH_2O\} + O_2 \xrightarrow{\text{Microorganisms}} CO_2 + H_2O \qquad (12.9.1)$$

Unless the water is reaerated efficiently, as by turbulent flow in a shallow stream, it rapidly loses oxygen and will not support higher forms of aquatic life.

In addition to the microorganism-mediated oxidation of organic matter, oxygen in water may be consumed by the biooxidation of nitrogenous material,

$$NH_4^+ + 2O_2 \rightarrow 2H^+ + NO_3^- + H_2O \qquad (12.9.2)$$

and by the chemical or biochemical oxidation of chemical reducing agents:

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3(s) + 8H^+ \qquad (12.9.3)$$

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-} \qquad (12.9.4)$$

All these processes contribute to the deoxygenation of water.

The degree of oxygen consumption by microbially mediated oxidation of contaminants in water is called the **biochemical oxygen demand** (or biological oxygen demand), **BOD**. This parameter is commonly measured by determining the quantity of oxygen utilized by suitable aquatic microorganisms during a five-day period. Despite the somewhat arbitrary five-day period, this test remains a respectable measure of the short-term oxygen demand exerted by a pollutant.[1]

The addition of oxidizable pollutants to streams produces a typical oxygen sag curve as shown in Figure 12.3. Initially, a well-aerated, unpolluted stream is relatively free of oxidizable material; the oxygen level is high; and the bacterial

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population is relatively low. With the addition of oxidizable pollutant, the oxygen level drops because reaeration cannot keep up with oxygen consumption. In the decomposition zone, the bacterial population rises. The septic zone is characterized by a high bacterial population and very low oxygen levels. The septic zone terminates when the oxidizable pollutant is exhausted, and then the recovery zone begins. In the recovery zone, the bacterial population decreases and the dissolved oxygen level increases until the water regains its original condition.

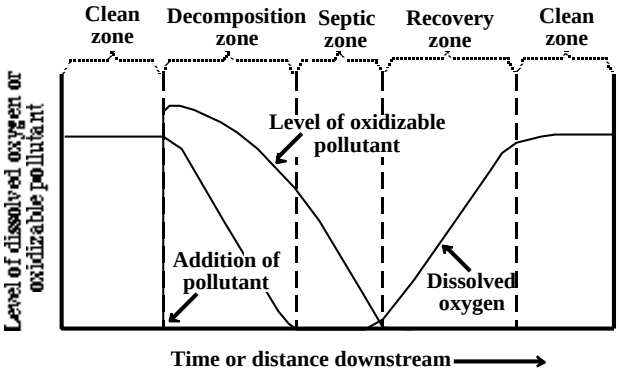


Figure 12.3 Oxygen sag curve resulting from the addition of oxidizable pollutant material to a stream.

Although BOD is a reasonably realistic measure of water quality insofar as oxygen is concerned, the test for determining it is time-consuming and cumbersome to perform. Total organic carbon (TOC), is frequently measured by catalytically oxidizing carbon in the water and measuring the CO_2 that is evolved. It has become popular because TOC is readily determined instrumentally.

12.10 ORGANIC POLLUTANTS

Sewage

As shown in Table 12.4, sewage from domestic, commercial, food-processing, and industrial sources contains a wide variety of pollutants, including organic pollutants. Some of these pollutants, particularly oxygen-demanding substances (see Section 12.9)—oil, grease, and solids—are removed by primary and secondary sewage-treatment processes. Others, such as salts, heavy metals, and refractory (degradation-resistant) organics, are not efficiently removed.

Disposal of inadequately treated sewage can cause severe problems. For example, offshore disposal of sewage, once commonly practiced by coastal cities, results in the formation of beds of sewage residues. Municipal sewage typically contains about 0.1% solids, even after treatment, and these settle out in the ocean in a typical pattern, illustrated in Figure 12.4. The warm sewage water rises in the cold hypolimnion and is carried laterally by tides or currents. Rising to the thermocline, it spreads out as a cloud from which the solids rain down on the ocean floor. Aggregation of sewage colloids is aided by dissolved salts in seawater, thus promoting the formation of sludge-containing sediment.

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Table 12.4 Some of the Primary Constituents of Sewage from a City Sewage System

Constituent	Potential sources	Effects in water
Oxygen-demanding substances	Mostly organic materials, particularly human feces	Consume dissolved oxygen
Refractory organics	Industrial wastes, household products	Toxic to aquatic life
Viruses	Human wastes	Cause disease (possibly cancer); major deterrent to sewage recycle through water systems
Detergents	Household detergents	Esthetics, prevent grease and oil removal, toxic to aquatic life
Phosphates	Detergents	Algal nutrients
Grease and oil	Cooking, food processing, industrial wastes	Esthetics, harmful to some aquatic life
Salts	Human wastes, water softeners, industrial wastes	Increase water salinity
Heavy metals	Industrial wastes, chemical laboratories	Toxicity
Chelating agents	Some detergents, industdustrial wastes	Heavy metal ion solubilization and transport
Solids	All sources	Esthetics, harmful to aquatic life

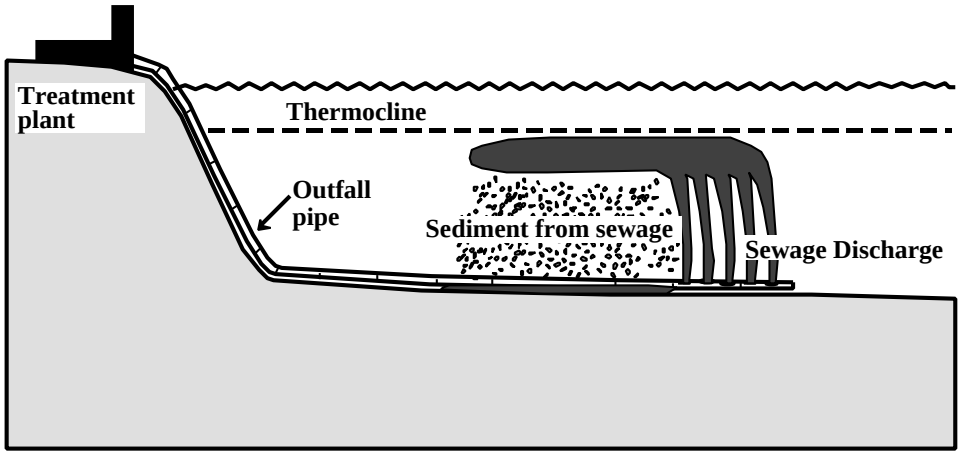


Figure 12.4 Settling of solids from an ocean-floor sewage effluent discharge.

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Another major disposal problem with sewage is the sludge produced as a product of the sewage treatment process (see Chapter 13). This sludge contains organic material that continues to degrade slowly; refractory organics; and heavy metals. The amounts of sludge produced are truly staggering. For example, the city of Chicago produces about 3 million tons of sludge each year. A major consideration in the safe disposal of such amounts of sludge is the presence of potentially dangerous components such as heavy metals.

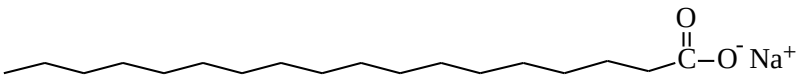
Careful control of sewage sources is needed to minimize sewage pollution problems. Particularly, heavy metals and refractory organic compounds need to be controlled at the source to enable use of sewage, or treated sewage effluents, for irrigation, recycling to the water system, or groundwater recharge.

Soaps, detergents, and associated chemicals are potential sources of organic pollutants. These pollutants are discussed briefly here.

Soaps, Detergents, and Detergent Builders

Soaps

Soaps are salts of higher fatty acids, such as sodium stearate, $C_{17}H_{35}COO^-Na^+$. Soap's cleaning action results largely from its emulsifying power and its ability to lower the surface tension of water. This concept can be understood by considering the dual nature of the soap anion. An examination of its structure shows that the stearate ion consists of an ionic carboxyl "head" and a long hydrocarbon "tail":



In the presence of oils, fats, and other water-insoluble organic materials, the tendency is for the "tail" of the anion to dissolve in the organic matter, whereas the "head" remains in aquatic solution. Thus, the soap emulsifies, or suspends, organic material in water. In the process, the anions form colloidal soap micelles in which the hydrocarbon "tails" of the soap anion are clustered inside the small colloidal particle and the carboxylate anion "heads" are located on the surface of the colloidal particle.

The primary disadvantage of soap as a cleaning agent comes from its reaction with divalent cations to form insoluble salts of fatty acids:

$$2C_{17}H_{35}COO^-Na^+ + Ca^{2+} \rightarrow Ca(C_{17}H_{35}CO_2)_2(s) + 2Na^+ \qquad (12.10.1)$$

These insoluble solids, usually salts of magnesium or calcium, are not at all effective as cleaning agents. In addition, the insoluble "curds" form unsightly deposits on clothing and in washing machines. If sufficient soap is used, all of the divalent cations can be removed by their reaction with soap, and the water containing excess soap will have good cleaning qualities. This is the approach commonly used when soap is employed with unsoftened water in the bathtub or wash basin, where the insoluble calcium and magnesium salts can be tolerated. However, in applications such as washing clothing, the water must be softened by

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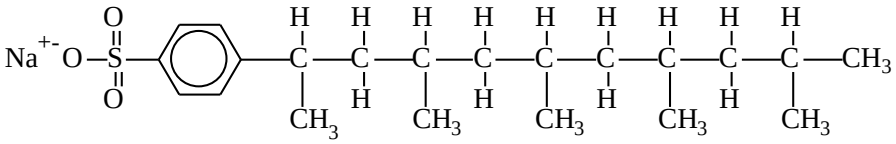
the removal of calcium and magnesium or their complexation by substances such as polyphosphates.

Although the formation of insoluble calcium and magnesium salts has resulted in the virtual elimination of soap as a cleaning agent for clothing, dishes, and most other materials, it has distinct advantages from the environmental standpoint. As soon as soap gets into sewage or an aquatic system, it generally precipitates as calcium and magnesium salts. Hence, any effects that soap might have in solution are eliminated. With eventual biodegradation, the soap is completely eliminated from the environment. Therefore, aside from the occasional formation of unsightly scum, soap does not cause any substantial pollution problems.

Detergents

Synthetic **detergents** have good cleaning properties and do not form insoluble salts with "hardness ions" such as calcium and magnesium. Such synthetic detergents have the additional advantage of being the salts of relatively strong acids and, therefore, they do not precipitate out of acidic waters as insoluble acids, an undesirable characteristic of soaps. The potential of detergents to contaminate water is high because of their heavy use throughout the consumer, institutional, and industrial markets. It has been projected that by 2004, about 3.0 billion pounds of detergent surfactants will be consumed in the U.S. household market alone, with slightly more consumed in Europe.[2] Most of this material, along with the other ingredients associated with detergent formulations, is discarded with wastewater.

The key ingredient of detergents is the **surfactant** or surface-active agent, which acts in effect to make water "wetter" and a better cleaning agent. Surfactants concentrate at interfaces of water with gases (air), solids (dirt), and immiscible liquids (oil). They do so because of their **amphiphilic structure**, meaning that one part of the molecule is a polar or ionic group (head) with a strong affinity for water, and the other part is a hydrocarbon group (tail) with an aversion to water. This kind of structure is illustrated below for the structure of alkyl benzene sulfonate (ABS) surfactant:

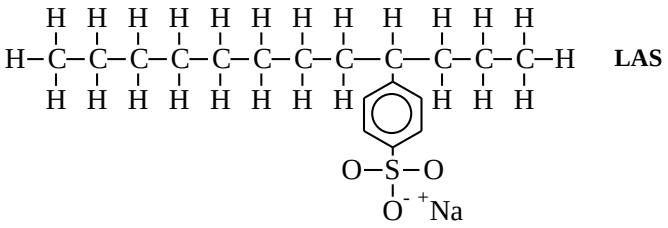


Until the early 1960s, ABS was the most common surfactant used in detergent formulations. However, it suffered the distinct disadvantage of being only very slowly biodegradable because of its branched-chain structure, which is particularly difficult for microorganisms to metabolize. The most objectionable manifestation of the nonbiodegradable detergents, insofar as the average citizen was concerned, was the "head" of foam that began to appear in glasses of drinking water in areas where sewage was recycled through the domestic water supply. Sewage-plant operators were disturbed by spectacular beds of foam that appeared near sewage outflows and in sewage treatment plants. Occasionally, the entire aeration tank of an activated sludge plant would be smothered by a blanket of foam. Among the other undesirable effects of persistent detergents upon waste-treatment processes were lowered surface

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tension of water; deflocculation of colloids; flotation of solids; emulsification of grease and oil; and destruction of useful bacteria. Consequently, ABS was replaced by a biodegradable surfactant known as linear alkyl sulfonate LAS.

LAS, α–benzenesulfonate, has the general structure



where the benzene ring may be attached at any point on the alkyl chain except at the ends. LAS is more biodegradable than ABS because the alkyl portion of LAS is not branched and does not contain the tertiary carbon that is so detrimental to biodegradability. Since LAS has replaced ABS in detergents, the problems arising from the surface-active agent in the detergents (such as toxicity to fish fingerlings) have greatly diminished and the levels of surface-active agents found in water have decreased markedly.

Most of the environmental problems currently attributed to detergents do not arise from the surface-active agents, which basically improve the wetting qualities of water. The **builders** added to detergents continued to cause environmental problems for a longer time, however. Builders bind to hardness ions, making the detergent solution alkaline and greatly improving the action of the detergent surfactant. A commercial solid detergent contains only 10–30% surfactant. In addition, some detergents still contain polyphosphates added to complex calcium and to function as builders. Other ingredients include ion exchangers, alkalies (sodium carbonate), anticorrosive sodium silicates, amide foam stabilizers, soil-suspending carboxymethylcellulose, bleaches, fabric softeners, enzymes, optical brighteners, fragrances, dyes, and diluent sodium sulfate. Of these materials, the polyphosphates have caused the most concern as environmental pollutants, although these problems have largely been resolved.

Increasing demands on the performance of detergents have led to a growing use of enzymes in detergent formulations destined for both domestic and commercial applications. To a degree, enzymes can take the place of chlorine and phosphates, both of which can have detrimental environmental consequences. Lipases and cellulases are the most useful enzymes for detergent applications.

Biorefractory Organic Pollutants

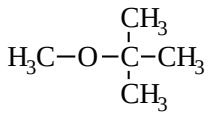
Millions of tons of organic compounds are manufactured globally each year. Significant quantities of several thousand such compounds appear as water pollutants. Most of these compounds, particularly the less biodegradable ones, are substances to which living organisms have not been exposed until recent years. Frequently, their effects upon organisms are not known, particularly for long-term exposures at very low levels. The potential of synthetic organics for causing genetic damage, cancer, or other ill effects is uncomfortably high. On the positive side,

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organic pesticides enable a level of agricultural productivity without which millions would starve. Synthetic organic chemicals are increasingly taking the place of natural products in short supply. Thus it is that organic chemicals are essential to the operation of a modern society. Because of their potential danger, however, acquisition of knowledge about their environmental chemistry must have a high priority.

Biorefractory organics are the organic compounds of most concern in wastewater, particularly when they are found in sources of drinking water. These are poorly biodegradable substances, prominent among which are aromatic or chlorinated hydrocarbons. Included in the list of biorefractory organic industrial wastes are benzene, bornyl alcohol, bromobenzene, bromochlorobenzene, butylbenzene, camphor chloroethyl ether, chloroform, chloromethylethyl ether, chloronitrobenzene, chloropyridine, dibromobenzene, dichlorobenzene, dichloroethyl ether, dinitrotoluene, ethylbenzene, ethylene dichloride, 2-ethylhexanol, isocyanic acid, isopropylbenzene, methylbiphenyl, methyl chloride, nitrobenzene, styrene, tetrachloroethylene, trichloroethane, toluene, and 1,2-dimethoxybenzene. Many of these compounds have been found in drinking water, and some are known to cause taste and odor problems in water. Biorefractory compounds are not completely removed by biological treatment, and water contaminated with these compounds must be treated by physical and chemical means, including air stripping, solvent extraction, ozonation, and carbon adsorption.

Methyl *tert*-butyl ether (MTBE),



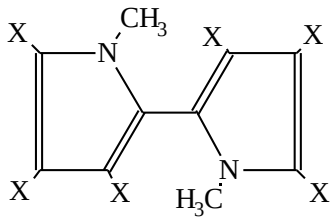
is now showing up as a low-level water pollutant in the U.S. This compound is added to gasoline as an octane booster and to decrease emissions of automotive exhaust air pollutants. A detailed study of the occurrence of MTBE in Donner Lake (California) showed significant levels of this pollutant, which spiked upward dramatically over a July 4 holiday.[3] They were attributed largely to emissions of unburned fuel from recreational motorboats and personal watercraft having two-cycle engines that discharge their exhausts directly to the water. In 1999 the U.S. Environmental Protection Agency proposed phasing out the use of MTBE in gasoline, largely because of its potential to pollute water.

Naturally Occurring Chlorinated and Brominated Compounds

Although halogenated organic compounds in water, such as those discussed as pesticides in Section 12.11, are normally considered to be from anthropogenic sources, approximately 2400 such compounds have been identified from natural sources. These are produced largely by marine species, especially some kinds of red algae, probably as chemical defense agents. Some marine microorganisms, worms, sponges, and tunicates are also known to produce organochlorine and organobromine compounds. An interesting observation has been made of the possible bioaccumulation of a class of compounds with the formula $C_{10}H_6N_2Br_4Cl_2$ in several species of sea birds from the Pacific ocean region.[4] Although the structural formula

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of the compound could not be determined with certainty, mass spectral data indicate that it is 1,1'-dimethyl-tetrabromodichloro-2,2'-bipyrrole (below):



X is Br (4) and Cl (2)

12.11 PESTICIDES IN WATER

The introduction of DDT during World War II marked the beginning of a period of very rapid growth in pesticide use. Pesticides are employed for many different purposes. Chemicals used in the control of invertebrates include **insecticides**, **molluscicides** for the control of snails and slugs, and **nematicides** for the control of microscopic roundworms. Vertebrates are controlled by **rodenticides**, which kill rodents, **avicides** used to repel birds, and **piscicides** used in fish control. **Herbicides** are used to kill plants. Plant **growth regulators**, **defoliants**, and **plant desiccants** are used for various purposes in the cultivation of plants. **Fungicide**s are used against fungi, **bactericides** against bacteria, **slimicides** against slime-causing organisms in water, and **algicides** against algae. As of the mid-1990s, U.S. agriculture used about 365 million kg of pesticides per year, whereas about 900 million kg of insecticides were used in nonagricultural applications including forestry, landscaping, gardening, food distribution, and home pest control. Insecticide production has remained about level during the last three or four decades. However, insecticides and fungicides are the most important pesticides with respect to human exposure in food because they are applied shortly before or even after harvesting. Herbicide production has increased as chemicals have increasingly replaced cultivation of land in the control of weeds and now accounts for the majority of agricultural pesticides. The potential exists for large quantities of pesticides to enter water either directly, in applications such as mosquito control or indirectly, primarily from drainage of agricultural lands.

Natural Product Insecticides, Pyrethrins, and Pyrethroids

Several significant classes of insecticides are derived from plants. These include **nicotine** from tobacco, **rotenone** extracted from certain legume roots, and **pyrethrins** (see structural formulas in Figure 12.5). Because of the ways that they are applied and their biodegradabilities, these substances are unlikely to be significant water pollutants.

Pyrethrins and their synthetic analogs represent both the oldest and newest of insecticides. Extracts of dried chrysanthemum or pyrethrum flowers, which contain pyrethrin I and related compounds, have been known for their insecticidal properties for a long time, and may have even been used as botanical insecticides in China almost 2000 years ago. The most important commercial sources of insecticidal pyrethrins are chrysanthemum varieties grown in Kenya. Pyrethrins have several

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advantages as insecticides, including facile enzymatic degradation, which makes them relatively safe for mammals; ability to rapidly paralyze ("knock down") flying insects; and good biodegradability characteristics.

Synthetic analogs of the pyrethrins, **pyrethroids**, have been widely produced as insecticides during recent years. The first of these was allethrin, and another common example is fenvalerate (see structures in Figure 12.5).

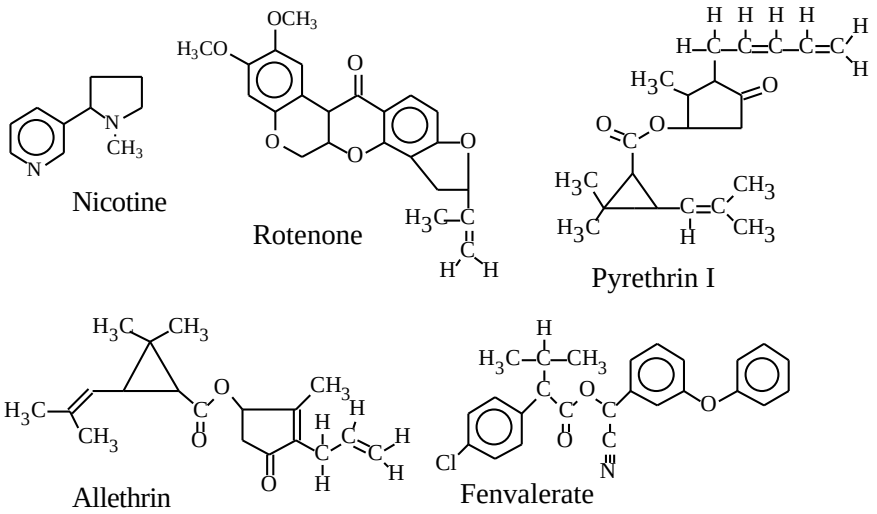


Figure 12.5 Common botanical insecticides and synthetic analogs of the pyrethrins.

DDT and Organochlorine Insecticides

Chlorinated hydrocarbon or organochlorine insecticides are hydrocarbon compounds in which various numbers of hydrogen atoms have been replaced by Cl atoms. The structural formulas of several chlorinated hydrocarbon insecticides are shown in Figure 12.6. It can be seen that the structural formulas of many of these insecticides are very similar; dieldrin and endrin are stereoisomers. The most commonly used insecticides in the 1960s, these compounds have been largely phased out of general use because of their toxicities, and particularly their accumulation and persistence in food chains. They are discussed briefly here, largely because of their historical interest, and because their residues in soils and sediments still contribute to water pollution.

Of the organochlorine insecticides, the most notable has been **DDT** (dichlorodiphenyltrichloroethane or 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane), which was used in massive quantities following World War II. It has a low acute toxicity to mammals, although there is some evidence that it might be carcinogenic. It is a very persistent insecticide and accumulates in food chains. It has been banned in the U.S. since 1972. For some time, **methoxychlor** was a popular DDT substitute, reasonably biodegradable, and with a low toxicity to mammals. Structurally similar **chlordane**, **aldrin**, **dieldrin/endrin**, and **heptachlor**, all now banned for application in the U.S., share common characteristics of high persistence and suspicions of potential carcinogenicity. **Toxaphene** is a mixture of up to 177 individual compounds produced by chlorination of camphene, a terpene isolated from pine trees, to give a

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material that contains about 68% Cl and has an empirical formula of $C_{10}H_{10}Cl_8$. This compound had the widest use of any agricultural insecticide, particularly on cotton. It was employed to augment other insecticides, especially DDT, and in later years methyl parathion. A mixture of five isomers, 1,2,3,4,5,6-hexachlorocyclohexane has been widely produced for insecticidal use. Only the gamma isomer is effective as an insecticide, whereas the other isomers give the product a musty odor and tend to undergo bioaccumulation. A formulation of the essentially pure gamma isomer has been marketed as the insecticide called **lindane**.

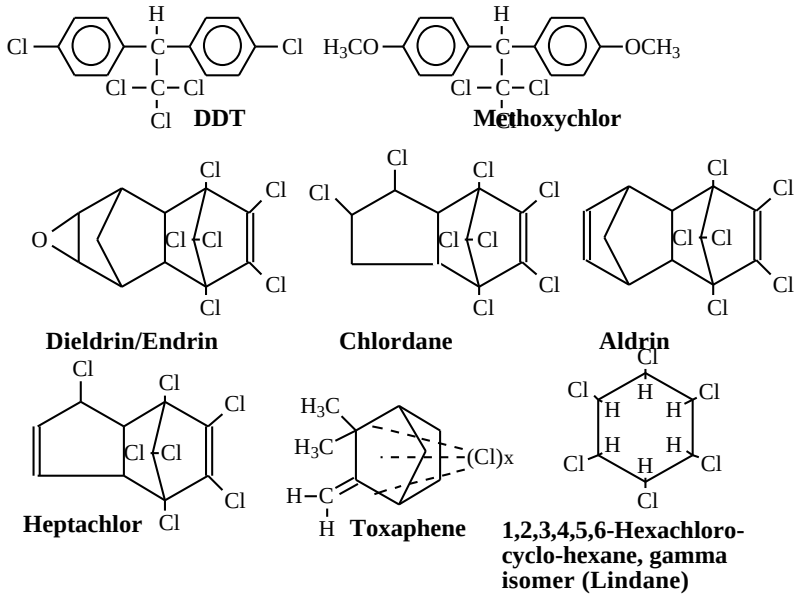
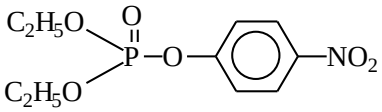


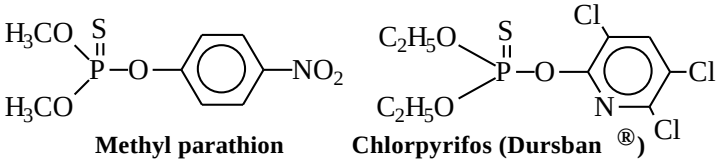
Figure 12.6 Common organochlorine insecticides.

Organophosphate Insecticides

Organophosphate insecticides are insecticidal organic compounds that contain phosphorus, some of which are organic esters of orthophosphoric acid, such as paraoxon:



More commonly, insecticidal phosphorus compounds are phosphorothionate compounds, such as parathion or chlorpyrifos,

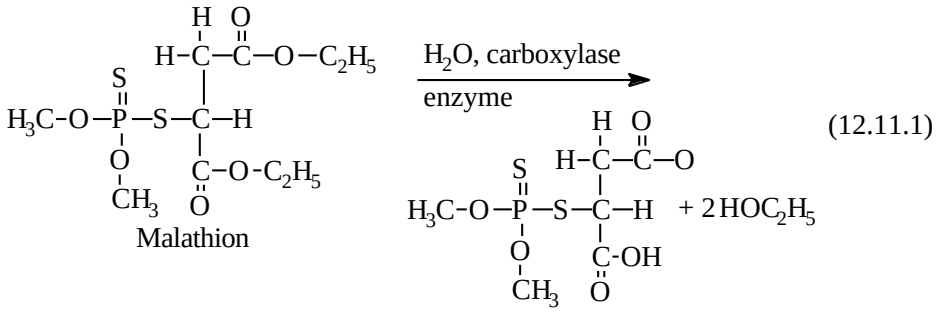


which have an =S group rather than an =O group bonded to P.

The toxicities of organophosphate insecticides vary a great deal. For example, as little as 120 mg of parathion has been known to kill an adult human, and a dose of

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only 2 mg has killed a child. Most accidental poisonings have occurred by absorption through the skin. Since its use began, several hundred people have been killed by parathion. In contrast, **malathion** shows how differences in structural formula can cause pronounced differences in the properties of organophosphate pesticides. Malathion has two carboxyester linkages that are hydrolyzable by carboxylase enzymes to relatively nontoxic products, as shown by the following reaction:



(12.11.1)

The enzymes that accomplish malathion hydrolysis are possessed by mammals, but not by insects, so mammals can detoxify malathion and insects cannot. The result is that malathion has selective insecticidal activity. For example, although malathion is a very effective insecticide, its LD_{50} (dose required to kill 50% of test subjects) for adult male rats is about 100 times that of parathion, reflecting the much lower mammalian toxicity of malathion compared with some of the more toxic organophosphate insecticides, such as parathion.

Unlike the organohalide compounds they largely displaced, the organophosphates readily undergo biodegradation and do not bioaccumulate. Because of their high biodegradability and restricted use, organophosphates are of comparatively little significance as water pollutants.

Carbamates

Pesticidal organic derivatives of carbamic acid, for which the formula is shown in Figure 12.7, are known collectively as **carbamates**. Carbamate pesticides have been widely used because some are more biodegradable than the formerly popular organochlorine insecticides, and have lower dermal toxicities than most common organophosphate pesticides.

Carbaryl has been widely used as an insecticide on lawns or gardens. It has a low toxicity to mammals. **Carbofuran** has a high water solubility and acts as a plant systemic insecticide. As such, it is taken up by the roots and leaves of plants so that insects are poisoned by the plant material on which they feed. **Pirimicarb** has been widely used in agriculture as a systemic aphicide. Unlike many carbamates, it is rather persistent, with a strong tendency to bind to soil.

The toxic effects of carbamates to animals are due to the fact that these compounds inhibit acetylcholinesterase. Unlike some of the organophosphate insecticides, they do so without the need for undergoing a prior biotransformation and are therefore classified as direct inhibitors. Their inhibition of acetylcholinesterase is relatively reversible. Loss of acetylcholinesterase inhibition activity may result from hydrolysis of the carbamate ester, which can occur metabolically.

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Herbicides

Herbicides are applied over millions of acres of farmland worldwide and are widespread water pollutants as a result of this intensive use. A 1994 report by the private Environmental Working Group indicated the presence of herbicides in 121 Midwestern U.S. drinking water supplies.[5] The herbicides named were atrazine, simazine, cyanazine, metolachlor, and alachlor, of which the first three are the most widely used. These substances are applied to control weeds on corn and soybeans, and the communities most affected were in the "Corn Belt" states of Kansas, Nebraska, Iowa, Illinois, and Missouri. The group doing the study applied the EPA's strictest standard for pesticides in food to water to come up with an estimate of approximately 3.5 million people at additional risk of cancer from these pesticides in drinking water.

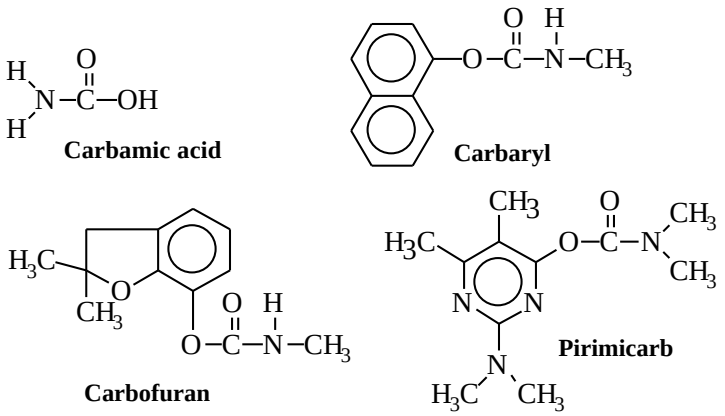


Figure 12.7 Carbamic acid and three insecticidal carbamates.

Bipyridilium Compounds

As shown by the structures in Figure 12.8, a bipyridilium compound contains 2 pyridine rings per molecule. The two important pesticidal compounds of this type are the herbicides **diquat** and **paraquat**, the structural formulas of which are illustrated below:

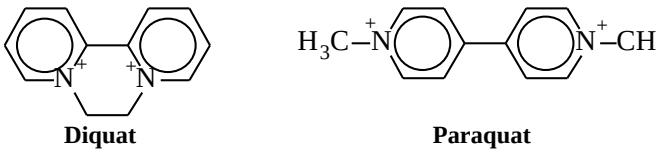


Figure 12.8 The two major bipyridilium herbicides (cation forms).

Other members of this class of herbicides include chlormequat, morfamquat, and difenzoquat. Applied directly to plant tissue, these compounds rapidly destroy plant cells and give the plant a frostbitten appearance. However, they bind tenaciously to soil, especially the clay mineral fraction, which results in rapid loss of herbicidal

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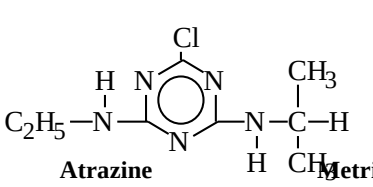
activity so that sprayed fields can be planted within a day or two of herbicide application.

Paraquat, which was registered for use in 1965, has been one of the most used of the bipyridilium herbicides. Highly toxic, it is reputed to have "been responsible for hundreds of human deaths."[6] Exposure to fatal or dangerous levels of paraquat can occur by all pathways, including inhalation of spray, skin contact, ingestion, and even suicidal hypodermic injections. Despite these possibilities and its widespread application, paraquat is used safely without ill effects when proper procedures are followed.

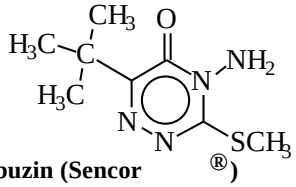
Because of its widespread use as a herbicide, the possibility exists of substantial paraquat contamination of food. Drinking water contamination by paraquat has also been observed.

Herbicidal Heterocyclic Nitrogen Compounds

A number of important herbicides contain three heterocyclic nitrogen atoms in ring structures and are therefore called **triazines**. Triazine herbicides inhibit photosynthesis. Selectivity is gained by the inability of target plants to metabolize and detoxify the herbicide. The longest established and common example of this class is atrazine, widely used on corn, and a widespread water pollutant in corn-growing regions. Another member of this class is metribuzin, which is widely used on soybeans, sugarcane, and wheat.



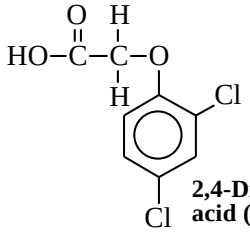
Atrazine



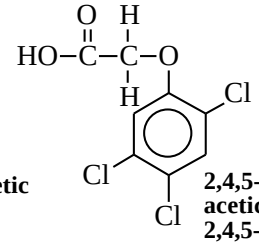
Metribuzin (Sencor®)

Chlorophenoxy Herbicides

The chlorophenoxy herbicides, including 2,4-D and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) shown below, were manufactured on a large scale for weed and brush control and as military defoliants. At one time, the latter was of particular concern because of contaminant TCDD (see below) present as a manufacturing byproduct.



2,4-Dichlorophenoxyacetic acid (and esters), 2,4-D



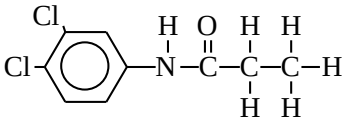
2,4,5-Trichlorophenoxy-acetic acid (and esters), 2,4,5-T

Substituted Amide Herbicides

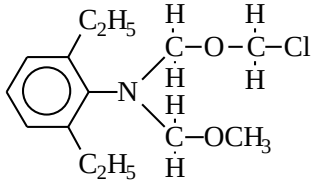
A diverse group of herbicides consists of substituted amides. Prominent among these are propanil, applied to control weeds in rice fields, and alachlor, marketed as

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Lasso® and widely applied to fields to kill germinating grass and broad-leaved weed seedlings:



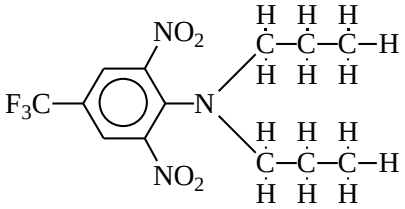
Propanil



Alachlor

Nitroaniline Herbicides

Nitroaniline herbicides are characterized by the presence of NO_2 and a substituted $–NH_2$ group on a benzene ring as shown for trifluralin:

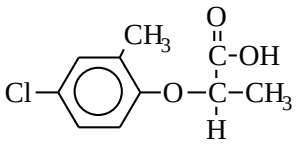


Trifluralin (Treflan®)

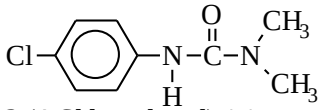
This class of herbicides is widely represented in agricultural applications and includes benefin (Balan®), oryzalin (Surflan®), pendimethalin (Prowl®), and fluchoralin (Basalin®).

Miscellaneous Herbicides

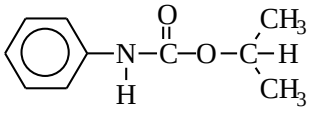
A wide variety of chemicals have been used as herbicides, and have been potential water pollutants. One such compound is R-mecoprop. Other types of herbicides include substituted ureas, carbamates, and thiocarbamates:



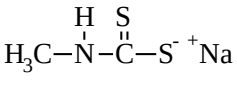
R-mecoprop



3-(4-Chlorophenyl)-1,1-dimethylurea (substituted urea)



Isopropyl carbanilate (a carbamate)

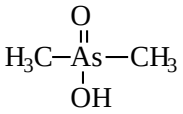


Sodium N-methyl-dithiocarbamate

Until about 1960, arsenic trioxide and other inorganic arsenic compounds (see Section 12.4) were employed to kill weeds. Because of the incredibly high rates of application of up to several hundred kilograms per acre, and because arsenic is nonbiodegradable, the potential still exists for arsenic pollution of surface water and

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groundwater from fields formerly dosed with inorganic arsenic. Organic arsenicals, such as cacodylic acid,

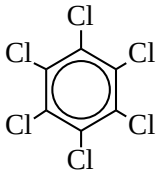


Hydroxydimethylarsine oxide, cacodylic acid

have also been widely applied to kill weeds.

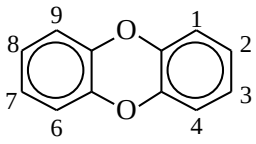
Byproducts of Pesticide Manufacture

A number of water pollution and health problems have been associated with the manufacture of organochlorine pesticides. For example, degradation-resistant hexachlorobenzene,

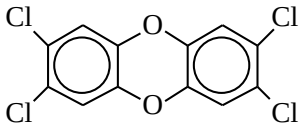


is used as a raw material for the synthesis of other pesticides and has often been found in water.

The most notorious byproducts of pesticide manufacture are **polychlorinated dibenzodioxins**. From 1 to 8 Cl atoms can be substituted for H atoms on dibenzo-*p*-dioxin (Figure 12.9), giving a total of 75 possible chlorinated derivatives. Commonly referred to as "dioxins," these species have a high environmental and toxicological significance. Of the dioxins, the most notable pollutant and hazardous waste compound is **2,3,7,8-tetrachlorodibenzo-*p*-dioxin** (**TCDD**), often referred to simply as "**dioxin**." This compound, which is one of the most toxic of all synthetic substances to some animals, was produced as a low-level contaminant in the manufacture of some aryl, oxygen-containing organohalide compounds such as chlorophenoxy herbicides (mentioned previously in this section) synthesized by processes used until the 1960s.



Dibenzo-*p*-dioxin



2,3,7,8-Tetrachlorodibenzo-*p*-dioxin

Figure 12.9 Dibenzo-*p*-dioxin and 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), often called simply "dioxin." In the structure of dibenzo-*p*-dioxin, each number refers to a numbered carbon atom to which an H atom is bound, and the names of derivatives are based upon the carbon atoms where another group has been substituted for the H atoms, as is seen by the structure and name of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin.

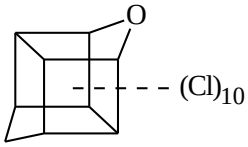
TCDD has a very low vapor pressure of only 1.7×10^{-6} mm Hg at 25°C, a high melting point of 305°C, and a water solubility of only 0.2 µg/L. It is stable thermally up to about 700°C, has a high degree of chemical stability, and is poorly biodegrad-

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able. It is very toxic to some animals, with an LD_{50} of only about 0.6 µg/kg body mass in male guinea pigs. (The type and degree of its toxicity to humans is largely unknown; it is known to cause a severe skin condition called chloracne). Because of its properties, TCDD is a \ persistent environmental pollutant and hazardous waste constituent of considerable concern. It has been identified in some municipal incineration emissions, in which it is believed to form when chlorine from the combustion of organochlorine compounds reacts with carbon in the incinerator.

TCDD has been a highly publicized environmental pollutant from improper waste disposal. The most notable case of TCDD contamination resulted from the spraying of waste oil mixed with TCDD on roads and horse arenas in Missouri in the early 1970s. The oil was used in an attempt to keep dust down in these areas. The extent of contamination was revealed by studies conducted in late 1982 and early 1983. As a result, the U.S. EPA bought out the entire TCDD-contaminated town of Times Beach, Missouri, in March 1983, at a cost of $33 million. Subsequently, permission was granted by the courts to incinerate the soil at Times Beach, as well as TCDD-contaminated soil from other areas at a total estimated cost of about $80 million. TCDD has been released in a number of industrial accidents, the most massive of which exposed several tens of thousands of people to a cloud of chemical emissions spread over an approximately 3-square-mile area at the Givaudan-La Roche Icmesa manufacturing plant near Seveso, Italy, in 1976. On an encouraging note from a toxicological perspective, no abnormal occurrences of major malformations were found in a study of 15,291 children born in the area within 6 years after the release.[7]

One of the greater environmental disasters ever to result from pesticide manufacture involved the production of Kepone, structural formula



This pesticide has been used for the control of banana-root borer, tobacco wireworm, ants, and cockroaches. Kepone exhibits acute, delayed, and cumulative toxicity in birds, rodents, and humans, and it causes cancer in rodents. It was manufactured in Hopewell, Virginia, during the mid-1970s. During this time, workers were exposed to Kepone and may have suffered health problems as a result. The plant was connected to the Hopewell sewage system, and frequent infiltration of Kepone wastes caused the Hopewell sewage treatment plant to become inoperative at times. As much as 53,000 kg of Kepone may have been dumped into the sewage system during the years the plant was operated. The sewage effluent was discharged to the James River, resulting in extensive environmental dispersion and toxicity to aquatic organisms. Decontamination of the river would have required dredging and detoxification of 135 million cubic meters of river sediment costing several billion dollars.

12.12 POLYCHLORINATED BIPHENYLS

First discovered as environmental pollutants in 1966, **polychlorinated biphenyls** (**PCB** compounds) have been found throughout the world in water, sedi-

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ments, bird tissue, and fish tissue. These compounds constitute an important class of special wastes. They are made by substituting from 1 to 10 Cl atoms onto the biphenyl aryl structure as shown on the left in Figure 12.10. This substitution can produce 209 different compounds (congeners), of which one example is shown on the right in Figure 12.10.

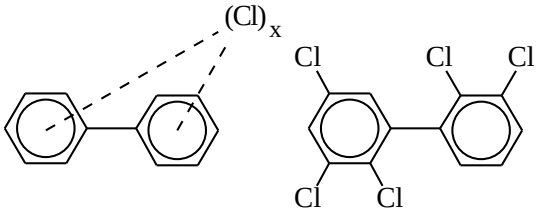


Figure 12.10 General formula of polychlorinated biphenyls (left, where X can range from 1 to 10) and a specific 5-chlorine congener (right).

Polychlorinated biphenyls have very high chemical, thermal, and biological stability; low vapor pressure; and high dielectric constants. These properties have led to the use of PCBs as coolant-insulation fluids in transformers and capacitors; for the impregnation of cotton and asbestos; as plasticizers; and as additives to some epoxy paints. The same properties that made extraordinarily stable PCBs so useful also contributed to their widespread dispersion and accumulation in the environment. By regulations issued in the U.S. under the authority of the Toxic Substances Control Act passed in 1976, the manufacture of PCBs was discontinued in the U.S., and their uses and disposal were strictly controlled.

Several chemical formulations have been developed to substitute for PCBs in electrical applications. Disposal of PCBs from discarded electrical equipment and other sources have caused problems, particularly since PCBs can survive ordinary incineration by escaping as vapors through the smokestack. However, they can be destroyed by special incineration processes.

PCBs are especially prominent pollutants in the sediments of the Hudson River as a result of waste discharges from two capacitor manufacturing plants that operated about 60 km upstream from the southernmost dam on the river from 1950 to 1976. The river sediments downstream from the plants exhibit PCB levels of about 10 ppm, 1–2 orders of magnitude higher than levels commonly encountered in river and estuary sediments.

Biodegradation of PCBs

The biodegradation of PCBs in New York's Hudson River provides an interesting example of microbial degradation of environmental chemicals. As a result of the dumping of PCBs in the Hudson River mentioned above, these virtually insoluble, dense, hydrophobic materials accumulated in the river's sediment, causing serious concern about their effects on water quality as a result of their bioaccumulation in fish. Methods of removal, such as dredging, were deemed prohibitively expensive and likely to cause severe contamination and disposal problems. Although it was well known that aerobic bacteria could degrade PCBs with only one or two Cl atom constituents, most of the PCB congeners discharged to the sediments had

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multiple chlorine atom constituents, specifically an average of 3.5 Cl atoms per PCB molecule at the time the PCBs were discharged. However, investigations during the late 1980s revealed that the PCBs in the sediments had been largely converted to mono- and dichloro-substituted forms. According to laboratory studies, this conversion can be carried out by the action of anaerobic bacteria.[8] , Once formed, the mono- and dichloro-substituted PCBs can be degraded by aerobic bacteria, which oxidize the PCB molecules, cleave the aromatic rings, and eventually mineralize the pollutants to inorganic chloride, carbon dioxide, and water.

Ideally, in the case of PCBs in sediments, about half of the work of remediation by biodegradation—conversion of highly substituted PCBs to molecules with one or two chlorines—is done by the slow, steady action of anaerobic bacteria without human intervention. Since the PCB products tend to stay in anaerobic surroundings, some assistance is required to provide oxygen to finish the biodegradation aerobically by introducing aerobic bacteria acclimated to PCB biodegradation, along with the oxygen and nutrients required for their growth.[9] Some authorities believe, however, that the processes described above will not occur to a significant extent under conditions that prevail in the sediments.

12.13 RADIONUCLIDES IN THE AQUATIC ENVIRONMENT

The massive production of **radionuclides** (radioactive isotopes) by weapons and nuclear reactors since World War II has been accompanied by increasing concern about the effects of radioactivity upon health and the environment. Radionuclides are produced as fission products of heavy nuclei of such elements as uranium or plutonium. They are also produced by the reaction of neutrons with stable nuclei. These phenomena are illustrated in Figure 12.11 and specific examples are given in Table 12.5. Radionuclides are formed in large quantities as waste products in nuclear power generation. Their ultimate disposal is a problem that has caused much controversy regarding the widespread use of nuclear power. Artificially produced radionuclides are also widely used in industrial and medical applications, particularly as

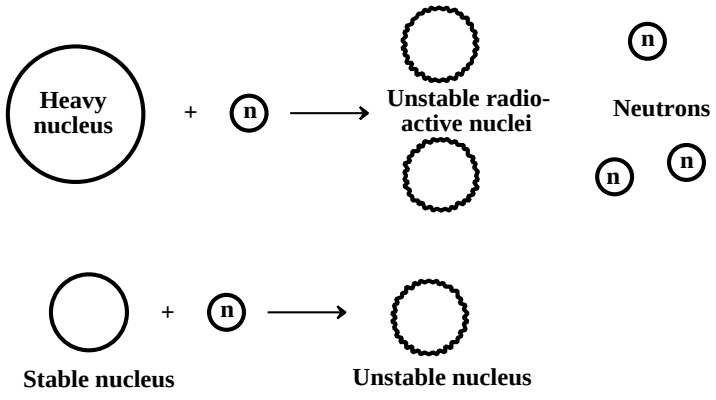


Figure 12.11 A heavy nucleus, such as that of ^{235}U, can absorb a neutron and break up (undergo fission), yielding lighter radioactive nuclei. A stable nucleus can absorb a neutron to produce a radioactive nucleus.

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Table 12.5 Radionuclides in Water

Radionuclide	Half-life	Nuclear reaction, description, source
Naturally occurring and from cosmic reactions		
Carbon-14	5730 y[1]	$^{14}N(n,p)^{14}C$,[2] thermal neutrons from cosmic or nuclear-weapon sources reacting with N_2
Silicon-32	~300 y	$^{40}Ar(p,x)^{32}Si$, nuclear spallation (splitting of the nucleus) of atmospheric argon by cosmic-ray protons
Potassium-40	~1.4×10^9 y	0.0119% of natural potassium including potassium in the body
Naturally occurring from ^{238}U series		
Radium-226	1620 y	Diffusion from sediments, atmosphere
Lead-210	21 y	$^{226}Ra \rightarrow$ 6 steps $\rightarrow {}^{210}Pb$
Thorium-230	75,200 y	$^{238}U \rightarrow$ 3 steps $\rightarrow {}^{230}Th$ produced *in situ*
Thorium-234	24 d	$^{238}U \rightarrow {}^{234}Th$ produced *in situ*
From reactor and weapons fission[3]		
Strontium-90 (28 y)	Iodine-131 (8 d)	Cesium-137 (30 y)
Barium-140 (13 d) > Zirconium-95 (65 d) >Cerium-141 (33d) > Strontium-89 (51 d) > Ruthenium-103 (40 d) > Krypton-85 (10.3 y)		
From nonfission sources		
Cobalt-60	5.25 y	From nonfission neutron reactions in reactors
Manganese-54	310 d	From nonfission neutron reactions in reactors
Iron-55	2.7 y	$^{56}Fe(n,2n)^{55}Fe$, from high-energy neutrons acting on iron in weapons hardware
Plutonium-239	24,300 y	$^{238}U(n,\gamma)^{239}Pu$, neutron capture by uranium

[1] Abbreviations: y, years; d, days

[2] This notation shows the isotope nitrogen-14 reacting with a neutron, n, giving off a proton, p, and forming the carbon-14 isotope; other nuclear reactions can be deduced from this notation where x represents nuclear fragments from spallation.

[3] The first three fission-product radioisotopes listed below as products of reactor and weapons fission are of most significance because of their high yields and biological activity. The other fission products are listed in generally decreasing order of yield.

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"tracers." With so many possible sources of radionuclides, it is impossible to entirely eliminate radioactive contamination of aquatic systems. Furthermore, radionuclides may enter aquatic systems from natural sources. Therefore, the transport, reactions, and biological concentration of radionuclides in aquatic ecosystems are of great importance to the environmental chemist.

Radionuclides differ from other nuclei in that they emit **ionizing radiation**—alpha particles, beta particles, and gamma rays. The most massive of these emissions is the **alpha particle**, a helium nucleus of atomic mass 4, consisting of two neutrons and two protons. The symbol for an alpha particle is $^{4}_{2}\alpha$. An example of alpha production is found in the radioactive decay of uranium-238:

$$^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}\alpha \qquad (12.13.1)$$

This transformation occurs when a uranium nucleus, atomic number 92 and atomic mass 238, loses an alpha particle, atomic number 2 and atomic mass 4, to yield a thorium nucleus, atomic number 90 and atomic mass 234.

Beta radiation consists of either highly energetic, negative electrons, which are designated $^{0}_{-1}\beta$, or positive electrons, called positrons, and designated $^{0}_{-1}\beta$. A typical beta emitter, chlorine-38, can be produced by irradiating chlorine with neutrons. The chlorine-37 nucleus, natural abundance 24.5%, absorbs a neutron to produce chlorine-38 and gamma radiation:

$$^{37}_{17}Cl + {}^{1}_{0}n \rightarrow {}^{38}_{17}Cl + \gamma \qquad (12.13.2)$$

The chlorine-38 nucleus is radioactive and loses a negative **beta particle** to become an argon-38 nucleus:

$$^{38}_{17}Cl \rightarrow {}^{38}_{18}Ar + {}^{0}_{-1}\beta \qquad (12.13.3)$$

Since the negative beta particle has essentially no mass and a -1 charge, the stable product isotope, argon-38, has the same mass and a charge 1 greater than chlorine-38.

Gamma rays are electromagnetic radiation similar to X-rays, though more energetic. Since the energy of gamma radiation is often a well-defined property of the emitting nucleus, it may be used in some cases for the qualitative and quantitative analysis of radionuclides.

The primary effect of alpha particles, beta particles, and gamma rays upon materials is the production of ions; therefore, they are called **ionizing radiation**. Due to their large size, alpha particles do not penetrate matter deeply, but cause an enormous amount of ionization along their short path of penetration. Therefore, alpha particles present little hazard outside the body, but are very dangerous when ingested. Although beta particles are more penetrating than alpha particles, they produce much less ionization per unit path length. Gamma rays are much more penetrating than particulate radiation, but cause much less ionization. Their degree of penetration is proportional to their energy.

The **decay** of a specific radionuclide follows first-order kinetics; that is, the number of nuclei disintegrating in a short time interval is directly proportional to the

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number of radioactive nuclei present. The rate of decay, $-dN/dt$, is given by the equation

$$\text{Decay rate} = -\frac{dN}{dt} = \lambda N \tag{12.13.4}$$

where N is the number of radioactive nuclei present and λ is the rate constant, which has units of reciprocal time. Since the exact number of disintegrations per second is difficult to determine in the laboratory, radioactive decay is often described in terms of the **activity**, A, which is proportional to the absolute rate of decay. The first-order decay equation can be expressed in terms of A,

$$A = A_0 e^{-\lambda t} \tag{12.13.5}$$

where A is the activity at time t; A_0 is the activity when t is zero; and e is the natural logarithm base. The **half-life**, $t_{1/2}$, is generally used instead of λ to characterize a radionuclide:

$$t_{1/2} = \frac{0.693}{\lambda} \tag{12.13.6}$$

As the term implies, a half-life is the period of time during which half of a given number of atoms of a specific kind of radionuclide decay. Ten half-lives are required for the loss of 99.9% of the activity of a radionuclide.

Radiation damages living organisms by initiating harmful chemical reactions in tissues. For example, bonds are broken in the macromolecules that carry out life processes. In cases of acute radiation poisoning, bone marrow that produces red blood cells is destroyed and the concentration of red blood cells is diminished. Radiation-induced genetic damage is of great concern. Such damage may not become apparent until many years after exposure. As humans have learned more about the effects of ionizing radiation, the dosage level considered to be safe has steadily diminished. For example, the United States Nuclear Regulatory Commission has dropped the maximum permissible concentration of some radioisotopes to levels of less than one ten-thousandth of those considered safe in the early 1950s. Although it is possible that even the slightest exposure to ionizing radiation entails some damage, some radiation is unavoidably received from natural sources. For the majority of the population, exposure to natural radiation exceeds that from artificial sources.

The study of the ecological and health effects of radionuclides involves consideration of many factors. Among these are the type and energy of radiation emitted and the half-life of the source. In addition, the degree to which the particular element is absorbed by living species and the chemical interactions and transport of the element in aquatic ecosystems are important factors. Radionuclides having very short half-lives may be hazardous when produced but decay too rapidly to affect the environment into which they are introduced. Radionuclides with very long half-lives may be quite persistent in the environment but of such low activity that little environmental damage is caused. Therefore, in general, radionuclides with intermediate half-lives are the most dangerous. They persist long enough to enter living systems while still retaining a high activity. Because they may be incorporated

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within living tissue, radionuclides of "life elements" are particularly dangerous. Much concern has been expressed over strontium-90, a common waste product of nuclear testing. This element is interchangeable with calcium in bone. Strontium-90 fallout drops onto pasture and crop land and is ingested by cattle. Eventually, it enters the bodies of infants and children by way of cow's milk.

Some radionuclides found in water, primarily radium and potassium-40, originate from natural sources, particularly leaching from minerals. Others come from pollutant sources, primarily nuclear power plants and testing of nuclear weapons. The levels of radionuclides found in water typically are measured in units of picocuries/liter, where a curie is 3.7×10^{10} disintegrations per second, and a picocurie is 1×10^{-12} that amount, or 3.7×10^{-2} disintegrations per second. (2.2 disintegrations per minute).

The radionuclide of most concern in drinking water is **radium**, Ra. Areas in the United States where significant radium contamination of water has been observed include the uranium-producing regions of the western U.S., Iowa, Illinois, Wisconsin, Missouri, Minnesota, Florida, North Carolina, Virginia, and the New England states.

The maximum contaminant level (MCL) for total radium (^{226}Ra plus ^{228}Ra) in drinking water is specified by the U.S. Environmental Protection Agency as 5 pCi/L (picocuries per liter). Perhaps as many as several hundred municipal water supplies in the U.S. exceed this level and require additional treatment to remove radium. Fortunately, conventional water softening processes, which are designed to take out excessive levels of calcium, are relatively efficient in removing radium from water.

As the use of nuclear power has increased, the possible contamination of water by fission-product radioisotopes has become more of a cause for concern. (If nations continue to refrain from testing nuclear weapons above ground, it is hoped that radioisotopes from this source will contribute only minor amounts of radioactivity to water.) Table 12.5 summarizes the major natural and artificial radionuclides likely to be encountered in water.

Transuranic elements are of growing concern in the oceanic environment. These alpha emitters are long-lived and highly toxic. As their production increases, so does the risk of environmental contamination. Included among these elements are various isotopes of neptunium, plutonium, americium, and curium. Specific isotopes, with half-lives in years given in parentheses, are: Np-237 (2.14×10^6); Pu-236 (2.85); Pu-238 (87.8); Pu-239 (2.44×10^4); Pu-240 (6.54×10^3); Pu-241 (15); Pu-242 (3.87×10^5); Am-241 (433); Am-243 (7.37×10^6); Cm-242 (0.22); and Cm-244 (17.9).

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Trace substances that are water pollutants are [1]_____ _____. The general types of water pollutants most likely to be involved with metal transport are [2]_____

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_____, and those most likely to be involved with eutrophication are [3]_____. Lead, cadmium and mercury are all examples of water pollutants called [4]_____, whereas arsenic is an example of [5]_____. One of these pollutants that is chemically very similar to zinc is [6]_____, one that potentially can get into water from plumbing made of it is [7]_____, and one that is converted by methylated organometallic forms by bacteria is [8] _____. A metalloid pollutant that occurs with phosphate minerals and enters into the environment along with some phosphorus compounds is [9]_____. The two major types of metal-organic interactions to be considered in an aquatic system are [10]_____. Of all the metals, [11]_____ has the greatest number of organometallic compounds in commercial use. Bactericidal, fungicidal, and insecticidal tributyl tin chloride and related tributyl tin (TBT) compounds are of particular environmental significance because of their widespread use as [12]_____ _____. Some classes and specific examples of inorganic water pollutants are [13]_____ _____. A highly toxic inorganic water pollutant that is widely used in certain mineral-processing operations is [14]_____. A water pollutant that is the initial product of the decay of nitrogenous organic wastes is [15]_____ _____ and one produced by bacteria acting on sulfate is [16]_____. A substance that causes lung cancer when inhaled, but which may not be particularly dangerous in drinking water is [17]_____. Eutrophication describes a condition of lakes or reservoirs involving [18]_____. Generally, the single plant nutrient that is generally named as the culprit in excessive eutrophication is [19]_____. The most common source of pollutant acid in water is [20]_____ formed by the microbial oxidation of [21]_____. Another water quality parameter discussed along with salinity that is, however, generally not introduced directly into water by human activity is [22]_____. The recharging of water softeners can introduce excessive amounts of [23]_____ into water. The overall biologically mediated reaction by which oxygen is consumed in water is [24]_____ _____. Biochemical oxygen demand is a measurement of [25]_____ _____. Primary and secondary sewage treatment processes remove [26]_____ from water. Substances that are especially troublesome in improperly disposed sewage sludge are [27]_____ _____. A soap anion exhibits a dual nature because it consists of [28]_____ _____ that likes water and a [29]_____ _____. Soap's primary disadvantage as a cleaning agent is [30]_____ _____. The surface-active agent, or surfactant, in detergents acts by [31]_____ _____. The advantage of LAS surface active agent over ABS is that the former is [32]_____. Most of the environmental problems that currently are associated with the use of detergents arise from the [33]_____ in detergents. Nonbio-

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degradable, low-molecular-weight organic compounds of low volatility are commonly called [34]_____. A once common gasoline additive that has been shown to pollute water is [35]_____. Chlorinated and brominated organic compounds that come from natural sources are generated primarily by [36]_____. Some general classes of pesticides are [37]_____ _____. Pesticides classified as "both the oldest and newest" kinds of pesticides are the pyrethrins and pyrethroids. Chemically, both parathion and malathion are classified as [38]_____ _____, but the latter is safer because [39]_____ _____. Although the toxicity of DDT to humans is low, it is environmentally damaging because of its [40]_____ _____. In the past, the most troublesome byproducts of pesticide manufacture were [41]_____ of which the most notorious example is [42]_____. A general and specific example of PCB structures are [43]_____. A transformer coolant fluid containing 50–70 percent PCBs is known as [44]_____. Two ways of producing radionuclides are [45]_____ _____. Radionuclides produce [46]_____ radiation in the three major forms of [47]_____. A time interval characteristic of radionuclides is called the [48]_____ defined as [49]_____ _____. Radiation damages living organisms by [50]_____ _____. In general, radionuclides with intermediate half-lives are the most dangerous because [51]_____ _____. The radionuclide of most concern in drinking water is [52]_____.

Answers to Chapter Summary

1. those that occur at levels of a few parts per million or less
2. metal-binding organic species
3. algal nutrients and detergents
4. heavy metals
5. metalloids
6. cadmium
7. lead
8. mercury
9. arsenic
10. complexation and organometallic compound formation
11. tin
12. industrial biocides
13. those that contribute acidity, alkalinity, or salinity to water; algal nutrients; cyanide ion; ammonia; carbon dioxide; hydrogen sulfide; nitrite; and sulfite
14. cyanide

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15. ammonia (ammonium ion)
16. hydrogen sulfide
17. asbestos
18. excess algal growth
19. phosphate
20. acid mine drainage
21. pyrite
22. alkalinity
23. salinity
24. $\{CH_2O\} + O_2 \xrightarrow{\text{Microorganisms}} CO_2 + H_2O$
25. the degree of oxygen consumption by microbially mediated oxidation of contaminants in water
26. oxygen-demanding substances, oil, grease, and solids
27. organic material that continues to degrade slowly, refractory organics, and heavy metals
28. an ionic carboxyl “head”
29. a long hydrocarbon “tail”
30. its reaction with divalent cations to form insoluble salts of fatty acids
31. lowering the surface tension of water to which the detergent is added, making the water “wetter”
32. biodegradable
33. builders
34. biorefractory
35. methyl *tert*-butyl ether
36. marine microorganisms
37. insecticides, molluscicides, nematicides, rodenticides, herbicides, plant growth regulators, defoliants, plant desiccants, fungicides, bactericides, and algicides
38. organophosphates
39. mammals can detoxify it
40. persistence and accumulation in food chains
41. polychlorinated dibenzodioxins
42. TCDD
43. structures shown in Figure 12.10
44. askarel
45. as fission products of heavy nuclei and by the reaction of neutrons with stable nuclei
46. ionizing
47. alpha particles, beta particles, and gamma rays
48. half-life
49. time during which half of a given number of atoms of a specific kind of radionuclide decay
50. initiating harmful chemical reactions in tissues
51. they persist long enough to enter living systems while still retaining a high activity
52. radium

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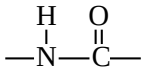
QUESTIONS AND PROBLEMS

1. Which of the following statements is true regarding chromium in water: (a) chromium(III) is suspected of being carcinogenic, (b) chromium(III) is less likely to be found in a soluble form than chromium(VI), (c) the toxicity of chromium(III) in electroplating wastewaters is decreased by oxidation to chromium(VI), (d) chromium is not an essential trace element, (e) chromium is known to form methylated species analogous to methylmercury compounds.

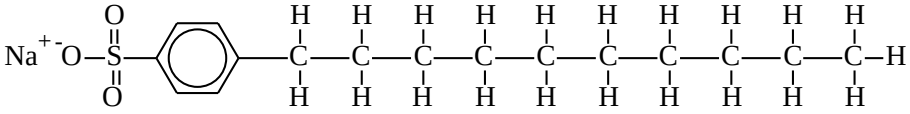
2. What do mercury and arsenic have in common in regard to their interactions with bacteria in sediments?

3. What are some characteristics of radionuclides that make them especially hazardous to humans?

4. To what class do pesticides containing the following group belong?



5. Consider the following compound:



Which of the following characteristics is not possessed by the compound: (a) one end of the molecule is hydrophilic and the other end is hydrophobic, (b) surface-active qualities, (c) the ability to lower surface tension of water, (d) good biodegradability, (e) tendency to cause foaming in sewage treatment plants.

6. A certain pesticide is fatal to fish fingerlings at a level of 0.50 parts per million in water. A leaking metal can containing 5.00 kg of the pesticide was dumped into a stream with a flow of 10.0 liters per second moving at 1 kilometer per

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hour. The container leaked pesticide at a constant rate of 5 mg/sec. For what distance (in km) downstream was the water contaminated by fatal levels of the pesticide by the time the container was empty?

7. Give a reason that Na_3PO_4 would not function well as a detergent builder, whereas $Na_3P_3O_{10}$ is satisfactory, though it is a source of pollutant phosphate.

8. Of the compounds $CH_3(CH_2)_{10}CO_2H$, $(CH_3)_3C(CH_2)_2CO_2H$, $CH_3(CH_2)_{10}CH_3$, and φ-$(CH_2)_{10}CH_3$ (where φ represents a benzene ring), which is the most readily biodegradable?

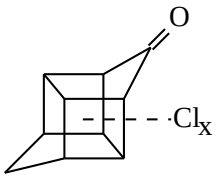
9. A pesticide sprayer got stuck while trying to ford a stream flowing at a rate of 136 liters per second. Pesticide leaked into the stream for exactly 1 hour and at a rate that contaminated the stream at a uniform 0.25 ppm of methoxychlor. How much pesticide was lost from the sprayer during this time?

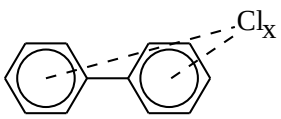
10. A sample of water contaminated by the accidental discharge of a radionuclide used for medicinal purposes showed an activity of 12,436 counts per second at the time of sampling and 8,966 cps exactly 30 days later. What is the half-life of the radionuclide?

11. What are the two reasons that soap is environmentally less harmful than ABS surfactant used in detergents?

12. What is the exact chemical formula of the specific compound designated as PCB?

13. Match each compound designated by a letter with the description corresponding to it designated by a number.

(a) CdS (b) $(CH_3)_2AsH$ (c) 

(d) 

(1) Pollutant released to a U.S. stream by a poorly controlled manufacturing process.

(2) Insoluble form of a toxic trace element likely to be found in anaerobic sediments.

(3) Common environmental pollutant formerly used as a transformer coolant.

(4) Chemical species thought to be produced by bacterial action.

14. A radioisotope has a nuclear half-life of 24 hours and a biological half-life of 16 hours (half of the element is eliminated from the body in 16 hours). A person accidentally swallowed sufficient quantities of this isotope to give an initial "whole body" count rate of 1000 counts per minute. What was the count rate after 16 hours?

15. What is the primary detrimental effect upon organisms of salinity in water arising from dissolved NaCl and Na_2SO_4?

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16. Give a specific example of each of the following general classes of water pollutants: (a) trace elements, (b) metal-organic combinations, (c) pesticides
17. A polluted water sample is suspected of being contaminated with one of the following: soap, ABS surfactant, or LAS surfactant. The sample has a very low BOD relative to its TOC. Which is the contaminant?

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Manahan, Stanley E. "WATER TREATMENT"
Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

13 WATER TREATMENT

13.1 WATER TREATMENT AND WATER USE

The treatment of water can be divided into three major categories:

- Purification for domestic use
- Treatment for specialized industrial applications
- Treatment of wastewater to make it acceptable for release or reuse

The type and degree of treatment are strongly dependent upon the source and intended use of the water. Water for domestic use must be thoroughly disinfected to eliminate disease-causing microorganisms, but may contain appreciable levels of dissolved calcium and magnesium (hardness). Water to be used in boilers may contain bacteria but must be quite soft to prevent scale formation. Wastewater being discharged into a large river may require less rigorous treatment than water to be reused in an arid region. As world demand for limited water resources grows, more sophisticated and extensive means will have to be employed to treat water.

Most physical and chemical processes used to treat water involve similar phenomena, regardless of their application to the three main categories of water treatment listed above. Therefore, after introductions to water treatment for municipal use, industrial use, and disposal, each major kind of treatment process is discussed as it applies to all of these applications.

13.2 MUNICIPAL WATER TREATMENT

The modern water treatment plant is often called upon to perform wonders with the water fed to it. The clear, safe, even tasteful water that comes from a faucet may have started as a murky liquid pumped from a polluted river laden with mud and swarming with bacteria. Or, its source may have been well water, much too hard for domestic use and containing high levels of stain-producing dissolved iron and man-

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ganese. The water treatment plant operator's job is to make sure that the water plant product presents no hazards to the consumer.

A schematic diagram of a typical municipal water treatment plant is shown in Figure 13.1. This particular facility treats water containing excessive hardness and a high level of iron. The raw water taken from wells first goes to an aerator. Contact of the water with air removes volatile solutes such as hydrogen sulfide, carbon dioxide, methane, and volatile odorous substances such as methane thiol (CH_3SH) and bacterial metabolites. Contact with oxygen also aids iron removal by oxidizing soluble iron(II) to insoluble iron(III). The addition of lime as CaO or $Ca(OH)_2$ after aeration raises the pH and results in the formation of precipitates containing the hardness ions Ca^{2+} and Mg^{2+}. These precipitates settle from the water in a primary basin. Much of the solid material remains in suspension and requires the addition of coagulants (such as iron(III) and aluminum sulfates, which form gelatinous metal hydroxides) to settle the colloidal particles. Activated silica or synthetic poly-electrolytes may also be added to stimulate coagulation or flocculation. The settling occurs in a secondary basin after the addition of carbon dioxide to lower the pH. Sludge from both the primary and secondary basins is pumped to a sludge lagoon. The water is finally chlorinated, filtered, and pumped to the city water mains.

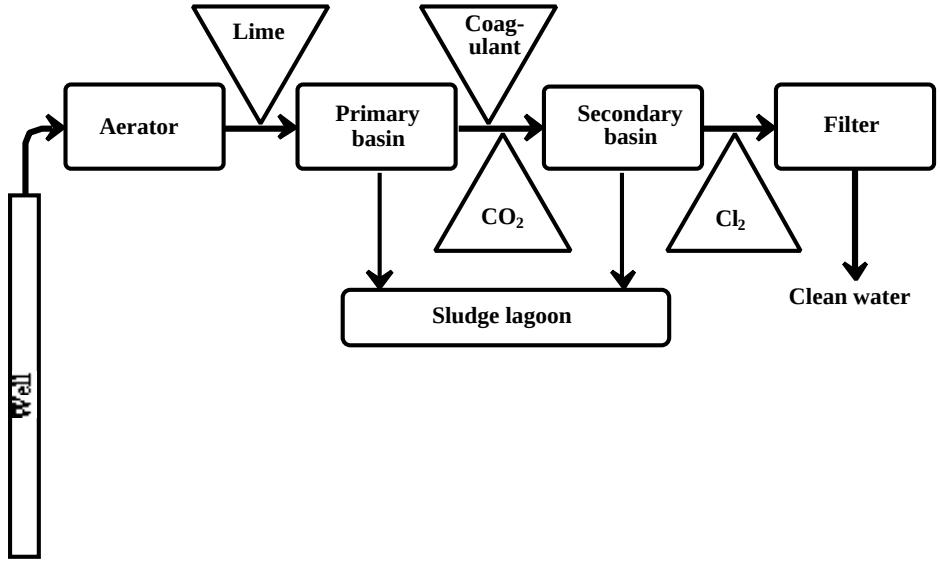


Figure 13.1 Schematic of a municipal water treatment plant.

13.3 TREATMENT OF WATER FOR INDUSTRIAL USE

Water is widely used in various process applications in industry. Other major industrial uses are boiler feedwater and cooling water. The kind and degree of treatment of water in these applications depends upon the end use. As examples, although cooling water may require only minimal treatment, removal of corrosive substances and scale-forming solutes is essential for boiler feedwater, and water used in food processing must be free of pathogens and toxic substances. Improper treatment of water for industrial use can cause problems such as corrosion, scale formation,

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reduced heat transfer in heat exchangers, reduced water flow, and product contamination. These effects may cause reduced equipment performance or equipment failure, increased energy costs due to inefficient heat utilization or cooling, increased costs for pumping water, and product deterioration. Obviously, the effective treatment of water at minimum cost for industrial use is a very important area of water treatment.

Numerous factors must be taken into consideration in designing and operating an industrial water treatment facility. These include the following:

- Water requirement
- Quantity and quality of available water sources
- Sequential use of water (successive uses for applications requiring progressively lower water quality)
- Water recycle
- Discharge standards

The various specific processes employed to treat water for industrial use are discussed in later sections of this chapter. **External treatment**, usually applied to the plant's entire water supply, uses processes such as aeration, filtration, and clarification to remove material that might cause problems from water. Such substances include suspended or dissolved solids, hardness, and dissolved gases. Following this basic treatment, the water can be divided into different streams, some to be used without further treatment, and the rest to be treated for specific applications.

Internal treatment is designed to modify the properties of water for specific applications. Examples of internal treatment include the following:

- Reaction of dissolved oxygen with hydrazine or sulfite
- Addition of chelating agents to react with dissolved Ca^{2+} and prevent formation of calcium deposits
- Addition of precipitants, such as phosphate used for calcium removal
- Treatment with dispersants to inhibit scale
- Addition of inhibitors to prevent corrosion
- Adjustment of pH
- Disinfection for food processing uses or to prevent bacterial growth in cooling water

13.4 SEWAGE TREATMENT

Typical municipal sewage contains oxygen-demanding materials, sediments, grease, oil, scum, pathogenic bacteria, viruses, salts, algal nutrients, pesticides, refractory organic compounds, heavy metals, and an astonishing variety of flotsam ranging from children's socks to sponges. It is the job of the waste-treatment plant to remove as much of this material as possible.

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Several characteristics are used to describe sewage. These include turbidity (international turbidity units), suspended solids (ppm), total dissolved solids (ppm), acidity (H^+ ion concentration or pH), and dissolved oxygen (in ppm O_2). Biochemical oxygen demand is used as a measure of oxygen-demanding substances.

Current processes for the treatment of wastewater can be divided into three main categories of primary treatment, secondary treatment, and tertiary treatment, each of which is discussed separately. Also discussed are total wastewater treatment systems, based largely upon physical and chemical processes

Waste from a municipal water system is normally treated in a **publicly owned treatment works**, **POTW**. In the United States these systems are allowed to discharge only effluents that have attained a certain level of treatment, as mandated by Federal law.

Primary Waste Treatment

Primary treatment of wastewater consists of the removal of insoluble matter such as grit, grease, and scum from water. The first step in primary treatment normally is screening. Screening removes or reduces the size of trash and large solids that get into the sewage system. These solids are collected on screens and scraped off for subsequent disposal. Most screens are cleaned with power rakes. Comminuting devices shred and grind solids in the sewage. Particle size can be reduced to the extent that the particles can be returned to the sewage flow.

Grit in wastewater consists of such materials as sand and coffee grounds that do not biodegrade well and generally have a high settling velocity. **Grit removal** is practiced to prevent its accumulation in other parts of the treatment system, to reduce clogging of pipes and other parts, and to protect moving parts from abrasion and wear. Grit normally is allowed to settle in a tank under conditions of low flow velocity, and it is then scraped mechanically from the bottom of the tank.

Primary sedimentation removes both settleable and floatable solids. During primary sedimentation there is a tendency for flocculent particles to aggregate for better settling, a process that may be aided by the addition of chemicals. The material that floats in the primary settling basin is known collectively as grease. In addition to fatty substances, the grease consists of oils, waxes, free fatty acids, and insoluble soaps containing calcium and magnesium. Normally, some of the grease settles with the sludge and some floats to the surface, where it can be removed by a skimming device.

Secondary Waste Treatment by Biological Processes

The most obvious harmful effect of biodegradable organic matter in wastewater is BOD, consisting of a biochemical oxygen demand for dissolved oxygen by microorganism-mediated degradation of the organic matter. **Secondary wastewater treatment** is designed to remove BOD, usually by taking advantage of the same kind of biological processes that would otherwise consume oxygen in water receiving the wastewater. Secondary treatment by biological processes takes many forms but consists basically of the action of microorganisms provided with added oxygen degrading organic material in solution or in suspension until the BOD of the

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waste has been reduced to acceptable levels. The waste is oxidized biologically under conditions controlled for optimum bacterial growth, and at a site where this growth does not influence the environment.

One of the simplest biological waste treatment processes is the **trickling filter** (Fig. 13.2) in which wastewater is sprayed over rocks or other solid support material covered with microorganisms. The structure of the trickling filter is such that contact of the wastewater with air is allowed and degradation of organic matter occurs by the action of the microorganisms.

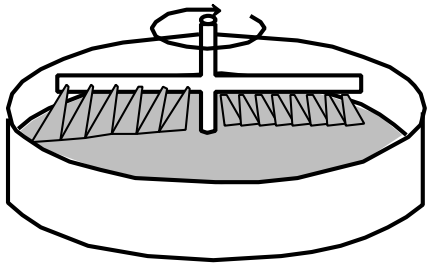


Figure 13.2 Trickling filter for secondary waste treatment.

Rotating biological reactors (**contactors**), another type of treatment system, consist of groups of large plastic discs mounted close together on a rotating shaft. The device is positioned such that at any particular instant half of each disc is immersed in wastewater and half exposed to air. The shaft rotates constantly, so that the submerged portion of the discs is always changing. The discs, usually made of high-density polyethylene or polystyrene, accumulate thin layers of attached biomass, which degrades organic matter in the sewage. Oxygen is absorbed by the biomass and by the layer of wastewater adhering to it during the time that the biomass is exposed to air.

Both trickling filters and rotating biological reactors are examples of fixed-film biological (FFB) or attached growth processes. The greatest advantage of these processes is their low energy consumption. The energy consumption is minimal because it is not necessary to pump air or oxygen into the water, as is the case with the popular activated sludge process described below. The trickling filter has long been a standard means of wastewater treatment, and a number of wastewater treatment plants use trickling filters at present.

The **activated sludge process**, Figure 13.3, is probably the most versatile and effective of all wastewater treatment processes. Microorganisms in the aeration tank convert organic material in wastewater to microbial biomass and CO_2. Organic nitrogen is converted to ammonium ion or nitrate. Organic phosphorus is converted to orthophosphate. The microbial cell matter formed as part of the waste degradation processes is normally kept in the aeration tank until the microorganisms are past the log phase of growth (Section 6.3), at which point the cells flocculate relatively well to form settleable solids. These solids settle out in a settler and a fraction of them is discarded. Part of the solids, the return sludge, is recycled to the head of the aeration tank and comes into contact with fresh sewage. The combination of a high concentration of “hungry” cells in the return sludge and a rich food source in the influent sewage provides optimum conditions for the rapid degradation of organic matter.

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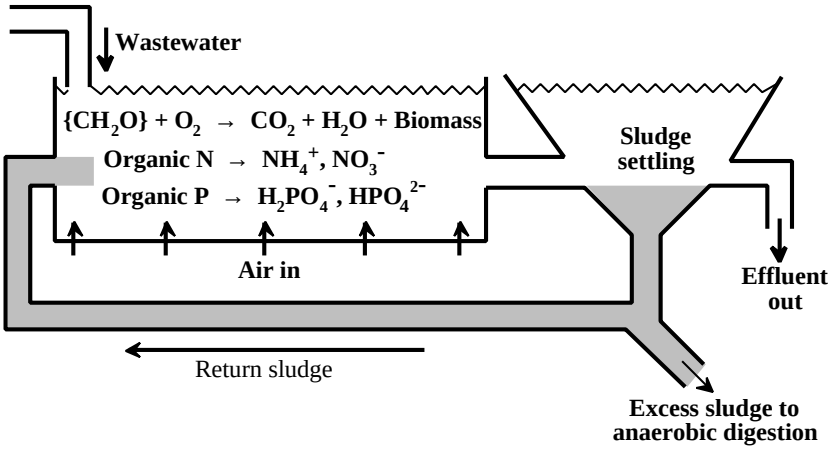


Figure 13.3 Activated sludge process.

The degradation of organic matter that occurs in an activated sludge facility also occurs in streams and other aquatic environments. However, in general, when a degradable waste is put into a stream, it encounters only a relatively small population of microorganisms capable of carrying out the degradation process. Thus, several days may be required for the buildup of a sufficient population of organisms to degrade the waste. In the activated sludge process, continual recycling of active organisms provides the optimum conditions for waste degradation, and a waste may be degraded within the very few hours that it is present in the aeration tank.

The activated sludge process provides two pathways for the removal of BOD, as illustrated schematically in Figure 13.4. BOD can be removed by (1) oxidation of organic matter to provide energy for the metabolic processes of the microorganisms, and (2) synthesis, incorporation of the organic matter into cell mass. In the first pathway, carbon is removed in the gaseous form as CO_2. The second pathway provides for removal of carbon as a solid in biomass. That portion of the carbon converted to CO_2 is vented to the atmosphere and does not present a disposal problem. The disposal of waste sludge, however, is a problem, primarily because it is only about 1% solids and contains many undesirable components. Normally, partial water removal is accomplished by drying on sand filters, vacuum filtration, or centrifugation. The dewatered sludge can be incinerated or used as landfill. To a certain extent, sewage

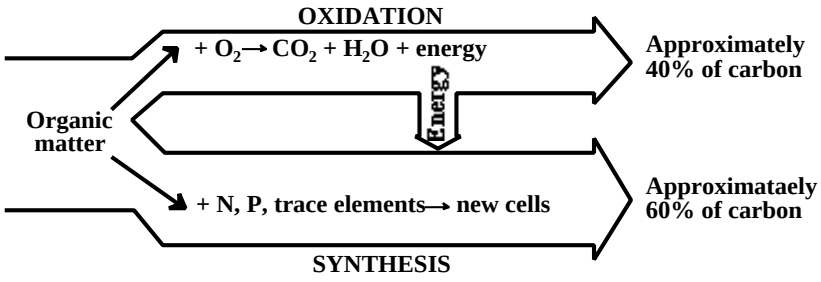


Figure 13.4 Pathways for the removal of BOD in biological wastewater treatment.

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sludge can be digested in the absence of oxygen by methane-producing anaerobic bacteria to produce methane and carbon dioxide

$$2\{CH_2O\} \rightarrow CH_4 + CO_2 \quad (13.4.1)$$

reducing both volatile-matter content and sludge volume by about 60%. A carefully designed plant can produce enough methane to provide for all of its power needs.

One of the most desirable means of sludge disposal is to use it to fertilize and condition soil. However, care has to be taken that excessive levels of heavy metals are not applied to the soil as sludge contaminants. Problems with various kinds of sludges resulting from water treatment are discussed further in Section 13.10.

Activated sludge wastewater treatment is the most common example of an aerobic suspended culture process. Many factors must be considered in the design and operation of an activated sludge wastewater treatment system.[1] These include parameters involved with the process modeling and kinetics. The microbiology of the system must be considered. In addition to BOD removal, phosphorus and nitrogen removal must also be taken into account. Oxygen transfer and solids separation are important. Industrial wastes and the fates and effects of industrial chemicals (xenobiotics) must also be considered.

Nitrification (the microbially mediated conversion of ammonium nitrogen to nitrate; see Section 6.11) is a significant process that occurs during biological waste treatment. Ammonium ion is normally the first inorganic nitrogen species produced in the biodegradation of nitrogenous organic compounds. It is oxidized, under the appropriate conditions, first to nitrite by *Nitrosomonas* bacteria, then to nitrate by *Nitrobacter*:

$$2NH_4^+ + 3O_2 \rightarrow 4H^+ + 2NO_2^- + 2H_2O \quad (13.4.2)$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^- \quad (13.4.3)$$

These reactions occur in the aeration tank of the activated sludge plant and are favored in general by long retention times, low organic loadings, large amounts of suspended solids, and high temperatures. Nitrification can reduce sludge settling efficiency because the denitrification reaction

$$4NO_3^- + 5\{CH_2O\} + 4H^+ \rightarrow 2N_2(g) + 5CO_2(g) + 7H_2O \quad (13.4.4)$$

occurring in the oxygen-deficient settler causes bubbles of N_2 to form on the sludge floc (aggregated sludge particles), making it so buoyant that it floats to the top. This prevents settling of the sludge and increases the organic load in the receiving waters. Under the appropriate conditions, however, advantage can be taken of this phenomenon to remove nutrient nitrogen from water (see Section 13.9).

Tertiary Waste Treatment

Unpleasant as the thought may be, many people drink used water—water that has been discharged from a municipal sewage treatment plant or from some

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industrial process. This raises serious questions about the presence of pathogenic organisms or toxic substances in such water. Because of high population density and heavy industrial development, the problem is especially acute in Europe, where some municipalities process 50% or more of their water from "used" sources. Obviously, there is a great need to treat wastewater in a manner that makes it amenable to reuse. This requires treatment beyond the secondary processes.

Tertiary waste treatment (sometimes called **advanced waste treatment**) is a term used to describe a variety of processes performed on the effluent from secondary waste treatment.[2] The contaminants removed by tertiary waste treatment fall into the general categories of (1) suspended solids, (2) dissolved organic compounds, and (3) dissolved inorganic materials, including the important class of algal nutrients. Each of these categories presents its own problems with regard to water quality. Suspended solids are primarily responsible for residual biological oxygen demand in secondary sewage effluent waters. The dissolved organics are the most hazardous from the standpoint of potential toxicity. The major problem with dissolved inorganic materials is that presented by algal nutrients, primarily nitrates and phosphates. In addition, potentially hazardous toxic metals may be found among the dissolved inorganics.

In addition to these chemical contaminants, secondary sewage effluent often contains a number of disease-causing microorganisms, requiring disinfection in cases where humans may later come into contact with the water. Among the bacteria that may be found in secondary sewage effluent are organisms causing tuberculosis, dysenteric bacteria (*Bacillus dysenteriae*, *Shigella dysenteriae*, *Shigella paradysenteriae*, *Proteus vulgaris*), cholera bacteria (*Vibrio cholerae*), bacteria causing mud fever (*Leptospira icterohemorrhagiae*), and bacteria causing typhoid fever (*Salmonella typhosa*, *Salmonella paratyphi*). In addition, viruses causing diarrhea, eye infections, infectious hepatitis, and polio may be encountered. Ingestion of sewage still causes disease, even in more-developed nations.

Physical-Chemical Treatment of Municipal Wastewater

Complete physical-chemical wastewater treatment systems offer both advantages and disadvantages relative to biological treatment systems. The capital costs of physical-chemical facilities can be less than those of biological treatment facilities, and they usually require less land. They are better able to cope with toxic materials and overloads. However, they require careful operator control and consume relatively large amounts of energy.

Basically, a physical-chemical treatment process involves:

- Removal of scum and solid objects
- Clarification, generally with addition of a coagulant, and frequently with the addition of other chemicals (such as lime for phosphorus removal)
- Filtration to remove filterable solids
- Activated carbon adsorption
- Disinfection

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The basic steps of a complete physical-chemical wastewater treatment facility are shown in Figure 13.5.

During the early 1970s, it appeared likely that physical-chemical treatment would largely replace biological treatment. However, higher chemical and energy costs since then have slowed the development of physical-chemical facilities.

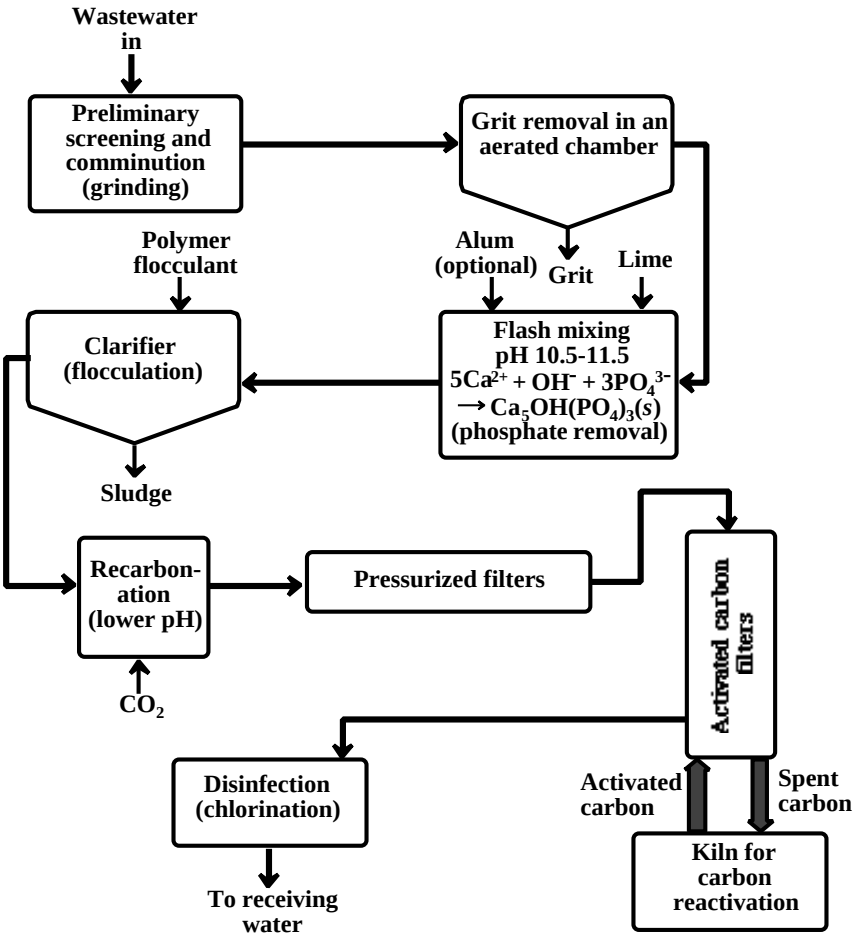


Figure 13.5 Major components of a complete physical-chemical treatment facility for municipal wastewater.

13.5 INDUSTRIAL WASTEWATER TREATMENT

Before treatment, industrial wastewater should be characterized fully and the biodegradability of wastewater constituents determined. The options available for the treatment of wastewater are summarized briefly in this section and discussed in greater detail in later sections.

One of two major ways of removing organic wastes is biological treatment by an activated sludge or related process (see Section 13.4 and Figure 13.3). It may be necessary to acclimate microorganisms to the degradation of constituents that are not

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normally biodegradable. Consideration needs to be given to possible hazards of biotreatment sludges, such as those containing excessive levels of heavy metal ions. The other major process for the removal of organics from wastewater is sorption by activated carbon (see Section 13.8), usually in columns of granular activated carbon. Activated carbon and biological treatment can be combined with the use of powdered activated carbon in the activated sludge process. The powdered activated carbon sorbs some constituents that may be toxic to microorganisms and is collected with the sludge. A major consideration with the use of activated carbon to treat wastewater is the hazard that spent activated carbon can present from the wastes it retains. These hazards may include those of toxicity or reactivity, such as those posed by wastes from the manufacture of explosives sorbed to activated carbon. Regeneration of the carbon is expensive and can be hazardous in some cases.

Wastewater can be treated by a variety of chemical processes, including acid/base neutralization, precipitation, and oxidation/reduction. Sometimes these steps must precede biological treatment; for example, acidic or alkaline wastewater must be neutralized for microorganisms to thrive in it. Cyanide in the wastewater can be oxidized with chlorine and organics with ozone, hydrogen peroxide promoted with ultraviolet radiation, or dissolved oxygen at high temperatures and pressures. Heavy metals can be precipitated with base, carbonate, or sulfide.

Wastewater can be treated by several physical processes. In some cases, simple density separation and sedimentation can be used to remove water-immiscible liquids and solids. Filtration is frequently required, and flotation by gas bubbles generated on particle surfaces may be useful. Wastewater solutes can be concentrated by evaporation, distillation, and membrane processes, including reverse osmosis, hyperfiltration, and ultrafiltration. Organic constituents can be removed by solvent extraction, air stripping, or steam stripping.

Synthetic resins are useful for removing some pollutant solutes from wastewater. Organophilic resins have proven useful for the removal of alcohols; aldehydes; ketones; hydrocarbons; chlorinated alkanes, alkenes, and aryl compounds; esters, including phthalate esters; and pesticides. Cation exchange resins are effective for the removal of heavy metals.

13.6 REMOVAL OF SOLIDS

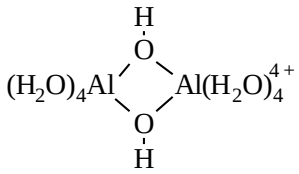
Relatively large solid particles are removed from water by simple **settling** and **filtration**. A special type of filtration procedure known as **microstraining** is especially effective in the removal of the very small particles. These filters are woven from stainless steel wire so fine that it is barely visible. This enables preparation of filters with openings only 60–70 μm across. These openings may be reduced to 5–15 μm by partial clogging with small particles, such as bacterial cells. The cost of this treatment is likely to be substantially lower than the costs of competing processes. High flow rates at low back pressures are normally achieved.

The removal of colloidal solids from water usually requires **coagulation**. Salts of aluminum and iron are the coagulants most often used in water treatment. Of these, alum or filter alum is most commonly used. This substance is a hydrated aluminum sulfate, $Al_2(SO_4)_3 \cdot 18H_2O$. When this salt is added to water, the aluminum ion hydrolyzes by reactions that consume alkalinity in the water, such as:

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$$Al(H_2O)_6^{3+} + 3HCO_3^- \rightarrow Al(OH)_3(s) + 3CO_2 + 6H_2O \quad (13.6.1)$$

The gelatinous hydroxide thus formed carries suspended material with it as it settles. Furthermore, it is likely that positively charged hydroxyl-bridged dimers such as



and higher polymers are formed that interact specifically with colloidal particles, bringing about coagulation. Sodium silicate partially neutralized by acid aids coagulation, particularly when used with alum. Metal ions in coagulants also react with virus proteins and destroy viruses in water.

Anhydrous iron(III) sulfate added to water forms iron(III) hydroxide in a reaction analogous to Reaction 13.6.1. An advantage of iron(III) sulfate is that it works over a wide pH range of approximately 4–11. Hydrated iron(II) sulfate, or copperas, $FeSO_4 \cdot 7H_2O$, is also commonly used as a coagulant. It forms a gelatinous precipitate of hydrated iron(III) oxide; in order to function, it must be oxidized to iron(III) by dissolved oxygen in the water at a pH higher than 13.5, or by chlorine, which can oxidize iron(II) at lower pH values.

Natural and synthetic polyelectrolytes are used in flocculating particles. Among the natural compounds so used are starch and cellulose derivatives, proteinaceous materials, and gums composed of polysaccharides. More recently, selected synthetic polymers, including neutral polymers and both anionic and cationic polyelectrolytes that are effective flocculants have come into use.

Coagulation-filtration is a much more effective procedure than filtration alone for the removal of suspended material from water. As the term implies, the process consists of the addition of coagulants that aggregate the particles into larger-size particles, followed by filtration. Either alum or lime, often with added polyelectrolytes, is most commonly employed for coagulation .

The filtration step of coagulation-filtration is usually performed on a medium such as sand or anthracite coal. Often, to reduce clogging, several media with progressively smaller interstitial spaces are used. One example is the **rapid sand filter**, which consists of a layer of sand supported by layers of gravel particles, the particles becoming progressively larger with increasing depth. The substance that actually filters the water is coagulated material that collects in the sand. As more material is removed, the buildup of coagulated material eventually clogs the filter and must be removed by back-flushing.

An important class of solids that must be removed from wastewater consists of suspended solids in secondary sewage effluent that arise primarily from sludge that was not removed in the settling process. These solids account for a large part of the BOD in the effluent and may interfere with other aspects of tertiary waste treatment, such as by clogging membranes in reverse osmosis water treatment processes. The quantity of material involved may be rather high. Processes designed to remove suspended solids often will remove 10–20 mg/L of organic material from secondary sewage effluent. In addition, a small amount of the inorganic material is removed.

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13.7 REMOVAL OF CALCIUM AND OTHER METALS

Calcium and magnesium salts, which generally are present in water as bicarbonates or sulfates, cause water hardness. One of the most common manifestations of water hardness is the insoluble "curd" formed by the reaction of soap with calcium or magnesium ions. The formation of these insoluble soap salts is discussed in Section 12.10. Although ions that cause water hardness do not form insoluble products with detergents, they do adversely affect detergent performance. Therefore, calcium and magnesium must be complexed or removed from water for detergents to function properly.

Another problem caused by hard water is the formation of mineral deposits. For example, when water containing calcium and bicarbonate ions is heated, insoluble calcium carbonate is formed:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + CO_2(g) + H_2O \quad (13.7.1)$$

This product coats the surfaces of hot water systems, clogging pipes and reducing heating efficiency. Dissolved salts such as calcium and magnesium bicarbonates and sulfates can be especially damaging in boiler feedwater. Clearly, the removal of water hardness is essential for many uses of water.

Several processes are used for softening water. On a large scale, such as in community water-softening operations, the lime-soda process is used. This process involves the treatment of water with lime, $Ca(OH)_2$, and soda ash, Na_2CO_3. Calcium is precipitated as $CaCO_3$ and magnesium as $Mg(OH)_2$. When the calcium is present primarily as "bicarbonate hardness," it can be removed by the addition of $Ca(OH)_2$ alone:

$$Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3(s) + 2H_2O \quad (13.7.2)$$

When bicarbonate ion is not present at substantial levels, a source of CO_3^{2-} must be provided at a high enough pH to prevent conversion of most of the carbonate to bicarbonate. These conditions are obtained by the addition of Na_2CO_3. For example, calcium present as the chloride can be removed from water by the addition of soda ash:

$$Ca^{2+} + 2Cl^- + 2Na^+ + CO_3^{2-} \rightarrow CaCO_3(s) + 2Cl^- + 2Na^+ \quad (13.7.3)$$

Note that the removal of bicarbonate hardness results in a net removal of soluble salts from solution, whereas removal of nonbicarbonate hardness involves the addition of at least as many equivalents of ionic material as are removed.

The precipitation of magnesium as the hydroxide requires a higher pH than the precipitation of calcium as the carbonate:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2(s) \quad (13.7.4)$$

The high pH required can be provided by the basic carbonate ion from soda ash:

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \quad (13.7.5)$$

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Some large-scale lime-soda softening plants make use of the precipitated calcium carbonate product as a source of additional lime. The calcium carbonate is first heated to at least 825˚C to produce quicklime, CaO:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2(g) \quad (13.7.6)$$

The quicklime is then slaked with water to produce calcium hydroxide:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (13.7.7)$$

The water softened by lime-soda softening plants usually suffers from two defects. First, because of super-saturation effects, some $CaCO_3$ and $Mg(OH)_2$ usually remain in solution. If not removed, these compounds will precipitate at a later time and cause harmful deposits or undesirable cloudiness in water. The second problem results from the use of highly basic sodium carbonate, which gives the product water an excessively high pH, up to pH 11. To overcome these problems, the water is recarbonated by bubbling CO_2 into it. The carbon dioxide converts the slightly soluble calcium carbonate and magnesium hydroxide to their soluble bicarbonate forms:

$$CaCO_3(s) + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \quad (13.7.8)$$

$$Mg(OH)_2(s) + 2CO_2 \rightarrow Mg^{2+} + 2HCO_3^- \quad (13.7.9)$$

The CO_2 also neutralizes excess hydroxide ion:

$$OH^- + CO_2 \rightarrow HCO_3^- \quad (13.7.10)$$

The pH generally is brought within the range 7.5-8.5 by recarbonation, commonly using CO_2 from the combustion of carbonaceous fuel. Scrubbed stack gas from a power plant frequently is utilized. Water adjusted to a pH, alkalinity, and Ca^{2+} concentration very close to $CaCO_3$ saturation is labeled *chemically stabilized*. It neither precipitates $CaCO_3$ in water mains, which can clog the pipes, nor dissolves protective $CaCO_3$ coatings from the pipe surfaces. Water with Ca^{2+} concentration much below $CaCO_3$ saturation is called an *aggressive* water.

Calcium can be removed from water very efficiently by the addition of orthophosphate:

$$5Ca^{2+} + 3PO_4^{3-} + OH^- \rightarrow Ca_5OH(PO_4)_3(s) \quad (13.7.11)$$

It should be pointed out that the chemical formation of a slightly soluble product for the removal of undesired solutes such as hardness ions, phosphate, iron, and manganese must be followed by sedimentation in a suitable apparatus. Frequently, coagulants must be added, and filtration employed for complete removal of these sediments.

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Water can be purified by ion exchange, the reversible transfer of ions between aquatic solution and a solid material capable of bonding ions. The removal of NaCl from solution by two ion exchange reactions is a good illustration of this process. First, the water is passed over a solid cation exchanger in the hydrogen form, represented by $H^{+-}\{Cat(s)\}$:

$$H^{+-}\{Cat(s)\} + Na^{+} + Cl^{-} \rightarrow Na^{+-}\{Cat(s)\} + H^{+} + Cl^{-} \quad (13.7.12)$$

Next, the water is passed over an anion exchanger in the hydroxide ion form, represented by $OH^{-+}\{An(s)\}$:

$$OH^{-+}\{An(s)\} + H^{+} + Cl^{-} \rightarrow Cl^{-+}\{An(s)\} + H_2O \quad (13.7.13)$$

Thus, the cations in solution are replaced by hydrogen ion and the anions by hydroxide ion, yielding water as the product.

The softening of water by ion exchange does not require the removal of all ionic solutes, just those cations responsible for water hardness. Generally, therefore, only a cation exchanger is necessary. Furthermore, the sodium rather than the hydrogen form of the cation exchanger is used, and the divalent cations are replaced by sodium ion. Sodium ion at low concentrations is harmless in water to be used for most purposes, and sodium chloride is a cheap and convenient substance with which to recharge the cation exchangers.

A number of materials have ion-exchanging properties. Among the minerals especially noted for their ion-exchange properties are the aluminum silicate minerals, or **zeolites**. An example of a zeolite that has been used commercially in water softening is glauconite, $K_2(MgFe)_2Al_6(Si_4O_{10})_3(OH)_{12}$. Synthetic zeolites have been prepared by drying and crushing the white gel produced by mixing solutions of sodium silicate and sodium aluminate.

The discovery in the mid-1930s of synthetic ion exchange resins composed of organic polymers with attached functional groups marked the beginning of modern ion-exchange technology. Structural formulas of typical synthetic ion exchangers are shown in Figures 13.6 and 13.7. The cation exchanger shown in Figure 13.6 is called a **strongly acidic cation exchanger** because the parent $-SO_3^{-}H^{+}$ group is a strong acid. When the functional group binding the cation is the $-CO_2^{-}$ group, the exchange resin is called a **weakly acidic cation exchanger**, because the $-CO_2H$ group is a weak acid. Figure 13.7 shows a **strongly basic anion exchanger** in which the functional group is a quaternary ammonium group, $-N^{+}(CH_3)_3$. In the hydroxide form, $-N^{+}(CH_3)_3OH^{-}$, the hydroxide ion is readily released, so the exchanger is classified as **strongly basic**.

The water-softening capability of a cation exchanger is shown in Figure 13.6, where sodium ion on the exchanger is exchanged for calcium ion in solution. The same reaction occurs with magnesium ion. Water softening by cation exchange is widely used, effective, and economical. However, it does cause some deterioration of wastewater quality arising from the contamination of wastewater by sodium chloride. Such contamination results from the periodic need to regenerate a water softener with sodium chloride in order to displace calcium and magnesium ions from the resin and replace these hardness ions with sodium ions:

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$$Ca^{2+}\,^{-}\{Cat(s)\}_2 + 2Na^+ + 2Cl^- \rightarrow 2Na^+\,^{-}\{Cat(s)\} + Ca^{2+} + 2Cl^- \qquad (13.7.14)$$

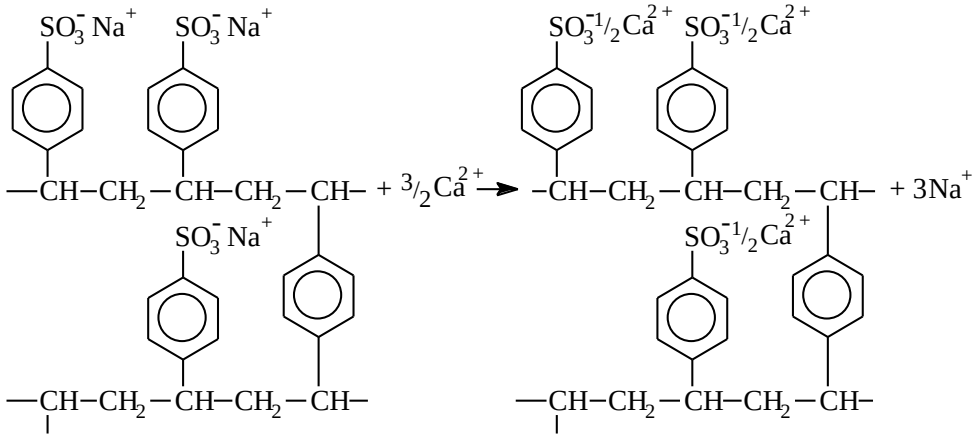


Figure 13.6. Strongly acidic cation exchanger. Sodium exchange for calcium in water is shown.

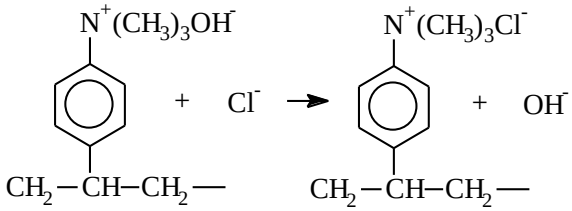


Figure 13.7 Strongly basic anion exchanger. Chloride exchange for hydroxide ion is shown.

During the regeneration process, a large excess of sodium chloride must be used — several pounds for a home water softener. Appreciable amounts of dissolved sodium chloride can be introduced into sewage by this route.

Strongly acidic cation exchangers are used for the removal of water hardness. Weakly acidic cation exchangers having the $-CO_2H$ group as a functional group are useful for removing alkalinity. Alkalinity generally is manifested by bicarbonate ion, a species that is a sufficiently strong base to neutralize the acid of a weak acid cation exchanger:

$$2R\text{-}CO_2H + Ca^{2+} + 2HCO_3^- \rightarrow [R\text{-}CO_2^-]_2Ca^{2+} + 2H_2O + 2CO_2 \qquad (13.7.15)$$

However, weak bases such as sulfate ion or chloride ion are not strong enough to remove hydrogen ion from the carboxylic acid exchanger. An additional advantage of these exchangers is that they can be regenerated almost stoichiometrically with dilute strong acids, thus avoiding the potential pollution problem caused by the use of excess sodium chloride to regenerate strongly acidic cation changers.

Chelation or, as it is sometimes known, *sequestration*, is an effective method of softening water without actually having to remove calcium and magnesium from solution. A complexing agent is added that greatly reduces the concentrations of free hydrated cations, as shown by some of the example calculations in Chapter 3. For example, chelating calcium ion with excess EDTA anion (Y^{4-}),

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$$Ca^{2+} + Y^{4-} \rightarrow CaY^{2-} \quad (13.7.16)$$

reduces the concentration of hydrated calcium ion, preventing the precipitation of calcium carbonate:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s) \quad (13.7.17)$$

Polyphosphate salts, EDTA, and NTA (see Chapter 3) are chelating agents commonly used for water softening. Polysilicates are used to complex iron.

Removal of Iron and Manganese

Soluble iron and manganese are found in many groundwaters because of reducing conditions that favor the soluble +2 oxidation state of these metals (see Chapter 4). Iron is the more commonly encountered of the two metals. In groundwater, the level of iron seldom exceeds 10 mg/L, and that of manganese is rarely higher than 2 mg/L. The basic method for removing both of these metals depends upon oxidation to higher insoluble oxidation states. The oxidation is generally accomplished by aeration. The rate of oxidation is pH-dependent in both cases, with a high pH favoring more rapid oxidation. The oxidation of soluble Mn(II) to insoluble MnO_2 is a complicated process. It appears to be catalyzed by solid MnO_2, which is known to adsorb Mn(II). This adsorbed Mn(II) is slowly oxidized on the MnO_2 surface.

Chlorine and potassium permanganate are sometimes employed as oxidizing agents for iron and manganese. There is some evidence that organic chelating agents with reducing properties hold iron(II) in a soluble form in water. In such cases, chlorine is effective because it destroys the organic compounds and enables the oxidation of iron(II).

In water with a high level of carbonate, $FeCO_3$ and $MnCO_3$ may be precipitated directly by raising the pH above 13.5 by the addition of sodium carbonate or lime. This approach is less popular than oxidation, however.

Relatively high levels of insoluble iron(III) and manganese(IV) frequently are found in water as colloidal material, which is difficult to remove. These metals can be associated with humic colloids or “peptizing” organic material that binds to colloidal metal oxides, stabilizing the colloid.

Heavy metals such as copper, cadmium, mercury, and lead are found in wastewaters from a number of industrial processes. Because of the toxicity of many heavy metals, their concentrations must be reduced to very low levels prior to release of the wastewater. A number of approaches are used in heavy-metals removal.

Lime treatment, discussed earlier in this section for calcium removal, precipitates heavy metals as insoluble hydroxides, basic salts, or coprecipitated with calcium carbonate or iron(III) hydroxide. This process does not completely remove mercury, cadmium, or lead, so their removal is aided by addition of sulfide (most heavy metals are sulfide-seekers):

$$Cd^{2+} + S^{2-} \rightarrow CdS(s) \quad (13.7.18)$$

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Heavy chlorination is frequently necessary to break down metal-solubilizing ligands (see Chapter 3). Lime precipitation does not normally permit recovery of metals and is sometimes undesirable from the economic viewpoint.

Electrodeposition (reduction of metal ions to metal by electrons at an electrode), *reverse osmosis* (see Section 13.9), and *ion exchange* are frequently employed for metal removal. Solvent extraction using organic-soluble chelating substances is also effective in removing many metals. **Cementation**, a process by which a metal deposits by reaction of its ion with a more readily oxidized metal, can be employed:

$$Cu^{2+} + Fe \text{ (iron scrap)} \rightarrow Fe^{2+} + Cu \qquad (13.7.19)$$

Activated carbon adsorption effectively removes some metals from water at the part per million level. Sometimes a chelating agent is sorbed to the charcoal to increase metal removal.

Even when not specifically designed for the removal of heavy metals, most waste-treatment processes remove appreciable quantities of the more troublesome heavy metals encountered in wastewater. Biological waste treatment effectively removes metals from water. These metals accumulate in the sludge from biological treatment, so sludge disposal must be given careful consideration.

Various physical-chemical treatment processes effectively remove heavy metals from wastewaters. One such treatment is lime precipitation followed by activated-carbon filtration. Activated-carbon filtration may also be preceded by treatment with iron(III) chloride to form an iron(III) hydroxide floc, which is an effective heavy metals scavenger. Similarly, alum, which forms aluminum hydroxide, may be added prior to activated-carbon filtration.

The form of the heavy metal has a strong effect upon the efficiency of metal removal. For instance, chromium(VI) is normally more difficult to remove than chromium(III). Chelation may prevent metal removal by solubilizing metals (see Chapter 3).

In the past, removal of heavy metals has been largely a fringe benefit of wastewater treatment processes. Currently, however, more consideration is being given to design and operating parameters that specifically enhance heavy-metals removal as part of wastewater treatment.

13.8 REMOVAL OF DISSOLVED ORGANICS

Very low levels of exotic organic compounds in drinking water are suspected of contributing to cancer and other maladies. Water disinfection processes, which by their nature involve chemically rather severe conditions, particularly of oxidation, have a tendency to produce **disinfection by-products**. Some of these are chlorinated organic compounds produced by chlorination of organics in water, especially humic substances. Removal of organics to very low levels prior to chlorination has been found to be effective in preventing trihalomethane formation. Another major class of disinfection by-products consists of organooxygen compounds such as aldehydes, carboxylic acids, and oxoacids.

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A variety of organic compounds survive, or are produced by, secondary wastewater treatment and should be considered as factors in discharge or reuse of the treated water. Almost half of these are humic substances (see Section 3.17) with a molecular-weight range of 1000–5000. Among the remainder are found ether-extractable materials, carbohydrates, proteins, detergents, tannins, and lignins. The humic compounds, because of their high molecular weight and anionic character, influence some of the physical and chemical aspects of waste treatment. The ether-extractables contain many of the compounds that are resistant to biodegradation and are of particular concern regarding potential toxicity, carcinogenicity, and mutagenicity. In the ether extract are found many fatty acids, hydrocarbons of the *n*-alkane class, naphthalene, diphenylmethane, diphenyl, methylnaphthalene, isopropylbenzene, dodecylbenzene, phenol, phthalates, and triethylphosphate.

The standard method for the removal of dissolved organic material is adsorption on activated carbon, a product that is produced from a variety of carbonaceous materials including wood, pulp-mill char, peat, and lignite.[3] The carbon is produced by charring the raw material anaerobically below 600˚C, followed by an activation step consisting of partial oxidation. Carbon dioxide can be employed as an oxidizing agent at 600–700˚C.

$$CO_2 + C \rightarrow 2CO \tag{13.8.1}$$

or the carbon can be oxidized by water at 800–900˚C:

$$H_2O + C \rightarrow H_2 + CO \tag{13.8.2}$$

These processes develop porosity, increase the surface area, and leave the C atoms in arrangements that have affinities for organic compounds.

Activated carbon comes in two general types: granulated activated carbon, consisting of particles 0.1–1 mm in diameter, and powdered activated carbon, in which most of the particles are 50–100 μm in diameter.

The exact mechanism by which activated carbon holds organic materials is not known. However, one reason for the effectiveness of this material as an adsorbent is its tremendous surface area. A solid cubic foot of carbon particles can have a combined pore and surface area of approximately 10 square miles!

Although interest is increasing in the use of powdered activated carbon for water treatment, currently granular carbon is more widely used. It can be employed in a fixed bed, through which water flows downward. Accumulation of particulate matter requires periodic backwashing. An expanded bed in which particles are kept slightly separated by water flowing upward can be used with less chance of clogging.

Economics require regeneration of the carbon. Regeneration can be accomplished by heating carbon to 950˚C in a steam-air atmosphere. This process oxidizes adsorbed organics and regenerates the carbon surface, with an approximately 10% loss of carbon.

Removal of organics can also be accomplished by adsorbent synthetic polymers. Such polymers as Amberlite XAD-4 have hydrophobic surfaces and strongly attract relatively insoluble organic compounds, such as chlorinated pesticides. The porosity of these polymers is up to 50% by volume, and the surface area may be as high as 850 m^2/g. They are readily regenerated by solvents such as isopropanol and acetone.

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Under appropriate operating conditions, these polymers remove virtually all nonionic organic solutes; for example, phenol at 250 mg/L is reduced to less than 0.1 mg/L by appropriate treatment with Amberlite XAD-4. The use of adsorbent polymers is more expensive than that of activated carbon, however.

Oxidation of dissolved organics holds some promise for their removal. Ozone, hydrogen peroxide, molecular oxygen (with or without catalysts), chlorine and its derivatives, permanganate, or ferrate (iron(VI)) can be used as oxidants. Electrochemical oxidation may be possible in some cases. High-energy electron beams produced by high-voltage electron accelerators also have the potential to destroy organic compounds.

Removal of Herbicides

Because of their widespread application and persistence, herbicides have proven to be particularly troublesome in some drinking water sources. Herbicide levels vary with season, related to times that they are applied to control weeds. The more soluble ones, such as chlorophenoxy esters, are most likely to enter drinking water sources. One of the most troublesome is atrazine, which is often manifested by its metabolite desethylatrazine. Activated carbon treatment is the best means of removing herbicides and their metabolites from drinking water sources.[4] A problem with activated carbon is that of **preloading**, in which natural organic matter in the water loads up the carbon and hinders uptake of pollutant organics such as herbicides. Pretreatment to remove such organic matter, such as flocculation and precipitation of humic substances, can significantly increase the efficacy of activated carbon for the removal of herbicides and other organics.

13.9 REMOVAL OF DISSOLVED INORGANICS

For complete water recycling to be feasible, inorganic-solute removal is essential. The effluent from secondary waste treatment generally contains 300–400 mg/L more dissolved inorganic material than does the municipal water supply. It is obvious, therefore, that 100% water recycling without removal of inorganics would cause the accumulation of an intolerable level of dissolved material. Even when water is not destined for immediate reuse, the removal of the inorganic nutrients phosphorus and nitrogen is highly desirable to reduce eutrophication downstream. In some cases, the removal of toxic trace metals is needed.

One of the most obvious methods for removing inorganics from water is distillation. However, the energy required for distillation is generally quite high, so that distillation is not generally economically feasible. Furthermore, volatile materials such as ammonia and odorous compounds are carried over to a large extent in the distillation process unless special preventive measures are taken. Freezing produces a very pure water, but is considered uneconomical with present technology. This leaves membrane processes as the most cost-effective means of removing inorganic materials from water. Membrane processes considered most promising for bulk removal of inorganics from water are electrodialysis, ion exchange, and reverse osmosis. (Other membrane processes used in water purification are nanofiltration, ultrafiltration,[5] microfiltration, and dialysis.)

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Electrodialysis

Electrodialysis consists of applying a direct current across a body of water separated into vertical layers by membranes alternately permeable to cations and anions.[6] Cations migrate toward the cathode and anions toward the anode. Cations and anions both enter one layer of water, and both leave the adjacent layer. Thus, layers of water enriched in salts alternate with those from which salts have been removed. The water in the brine-enriched layers is recirculated to a certain extent to prevent excessive accumulation of brine. The principles involved in electrodialysis treatment are shown in Figure 13.8.

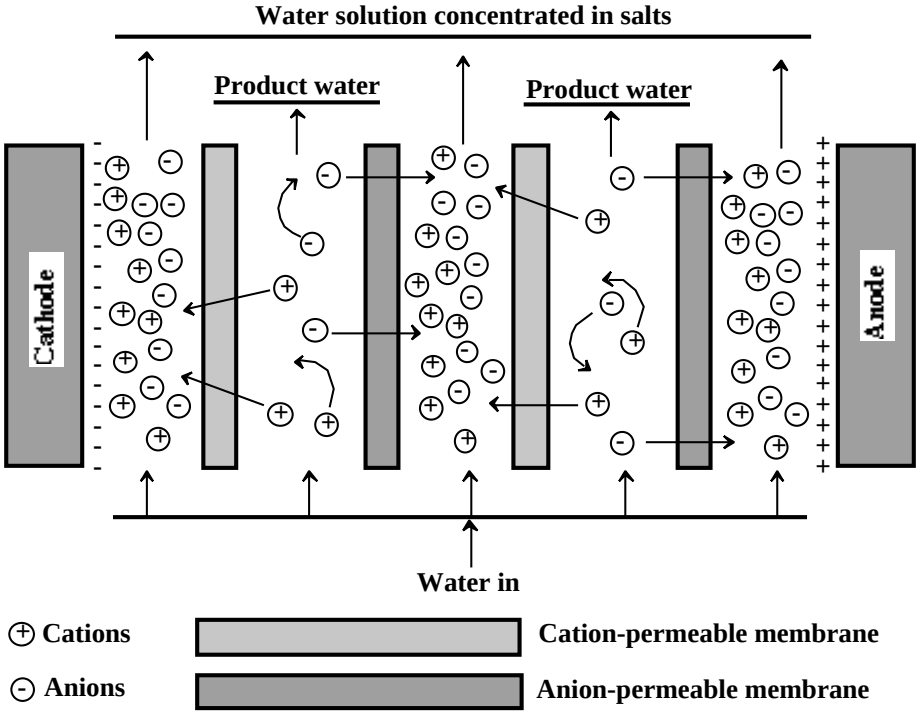


Figure 13.8 Electrodialysis apparatus for the removal of ionic material from water.

Fouling caused by various materials can cause problems with reverse osmosis treatment of water. Although the relatively small ions constituting the salts dissolved in wastewater readily pass through the membranes, large organic ions (proteins, for example) and charged colloids migrate to the membrane surfaces, often fouling or plugging the membranes and reducing efficiency. In addition, growth of microorganisms on the membranes can cause fouling.

Experience with pilot plants indicates that electrodialysis has the potential to be a practical and economical method to remove up to 50% of the dissolved inorganics from secondary sewage effluent after pretreatment to eliminate fouling substances. Such a level of efficiency would permit repeated recycling of water through municipal water systems without dissolved inorganic materials reaching unacceptably high levels.

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Ion Exchange

The ion exchange method for softening water is described in detail in Section 13.7. The ion exchange process used for removal of inorganics consists of passing the water successively over a solid cation exchanger and a solid anion exchanger, which replace cations and anions by hydrogen ion and hydroxide ion, respectively, so that each equivalent of salt is replaced by a mole of water. For the hypothetical ionic salt MX, the reactions are the following where $^{-}\{Cat(s)\}$ represents the solid cation exchanger and $^{+}\{An(s)\}$ represents the solid anion exchanger:

$$H^{+}\,^{-}\{Cat(s)\} + M^{+} + X^{-} \rightarrow M^{+}\,^{-}\{Cat(s)\} + H^{+} + X^{-} \quad (13.9.1)$$

$$OH^{-}\,^{+}\{An(s)\} + H^{+} + X^{-} \rightarrow X^{-}\,^{+}\{An(s)\} + H_2O \quad (13.9.2)$$

The cation exchanger is regenerated with strong acid and the anion exchanger with strong base.

Demineralization by ion exchange generally produces water of a very high quality. Unfortunately, some organic compounds in wastewater foul ion exchangers, and microbial growth on the exchangers can diminish their efficiency. In addition, regeneration of the resins is expensive, and the concentrated wastes from regeneration require disposal in a manner that will not damage the environment.

Reverse Osmosis

Reverse osmosis, Figure 13.9, is a very useful and well-developed technique for the purification of water.[7] Basically, it consists of forcing pure water through a semipermeable membrane that allows the passage of water but not of other material. This process, which is not simply sieve separation or ultrafiltration, depends on the preferential sorption of water on the surface of a porous cellulose acetate or polyamide membrane. Pure water from the sorbed layer is forced through pores in the membrane under pressure. If the thickness of the sorbed water layer is d, the pore diameter for optimum separation should be 2d. The optimum pore diameter depends upon the thickness of the sorbed pure water layer and may be several times the diameters of the solute and solvent molecules.

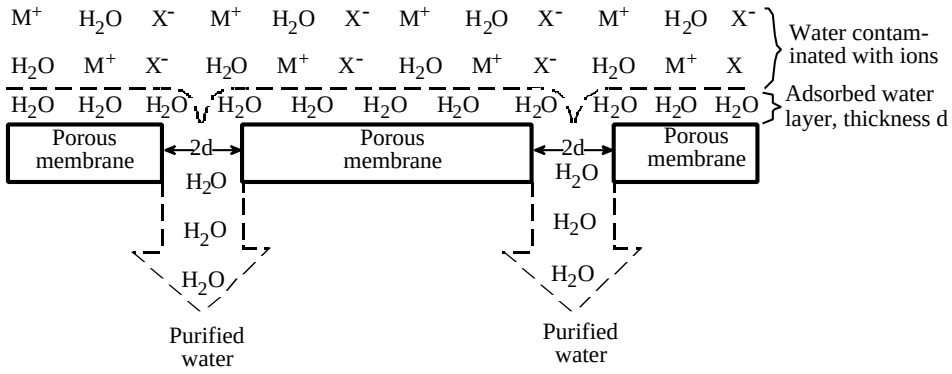


Figure 13.9 Solute removal from water by reverse osmosis.

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Phosphorus Removal

Advanced waste treatment normally requires removal of phosphorus to reduce algal growth. Algae may grow at PO_4^{3-} levels as low as 0.05 mg/L. Growth inhibition requires levels well below 0.5 mg/L. Since municipal wastes typically contain approximately 25 mg/L of phosphate (as orthophosphates, polyphosphates, and insoluble phosphates), the efficiency of phosphate removal must be quite high to prevent algal growth. This removal may occur in the sewage treatment process (1) in the primary settler; (2) in the aeration chamber of the activated sludge unit; or (3) after secondary waste treatment.

Activated sludge treatment removes about 20% of the phosphorus from sewage. Thus, an appreciable fraction of largely biological phosphorus is removed with the sludge. Detergents and other sources contribute significant amounts of phosphorus to domestic sewage and considerable phosphate ion remains in the effluent. However, some wastes, such as carbohydrate wastes from sugar refineries, are so deficient in phosphorus that supplementation of the waste with inorganic phosphorus is required for proper growth of the microorganisms degrading the wastes.

Under some sewage plant operating conditions, much greater than normal phosphorus removal has been observed. In such plants, characterized by high dissolved oxygen and high pH levels in the aeration tank, removal of 60–90% of the phosphorus has been attained, yielding two or three times the normal level of phosphorus in the sludge. In a conventionally operated aeration tank of an activated sludge plant, the CO_2 level is relatively high because of release of the gas by the degradation of organic material. A high CO_2 level results in a relatively low pH, due to the presence of carbonic acid. The aeration rate is generally not maintained at a very high level because oxygen is transferred relatively more efficiently from air when the dissolved oxygen levels in water are relatively low. Therefore, the aeration rate normally is not high enough to sweep out sufficient dissolved carbon dioxide to bring its concentration down to low levels. Thus, the pH generally is low enough that phosphate is maintained primarily in the form of the $H_2PO_4^-$ ion. However, at a higher rate of aeration in a relatively hard water, the CO_2 is swept out, the pH rises, and reactions such as the following occur:

$$5Ca^{2+} + 3HPO_4^{2-} + H_2O \rightarrow Ca_5OH(PO_4)_3(s) + 4H^+ \quad (13.9.3)$$

The precipitated hydroxyapatite or other form of calcium phosphate is incorporated in the sludge floc. Reaction 13.9.3 is strongly hydrogen ion-dependent, and an increase in the hydrogen ion concentration drives the equilibrium back to the left. Thus, under anaerobic conditions when the sludge medium becomes more acidic due to higher CO_2 levels, the calcium returns to solution.

Chemically, phosphate is most commonly removed by precipitation. Some common precipitants and their products are shown in Table 13.1. Precipitation processes are capable of at least 90–95% phosphorus removal at reasonable cost.Lime, $Ca(OH)_2$, is the chemical most commonly used for phosphorus removal:

$$5Ca(OH)_2 + 3HPO_4^{2-} \rightarrow Ca_5OH(PO_4)_3(s) + 3H_2O + 6OH^- \quad (13.9.4)$$

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Table 13.1 Chemical Precipitants for Phosphate and Their Products

Precipitant(s)	Products
$Ca(OH)_2$	$Ca_5OH(PO_4)_3$ (hydroxyapatite)
$Ca(OH)_2$ + NaF	$Ca_5F(PO_4)_3$ (fluorapatite)
$Al_2(SO_4)_3$	$AlPO_4$
$FeCl_3$	$FePO_4$
$MgSO_4$	$MgNH_4PO_4$

Lime has the advantages of low cost and ease of regeneration. The efficiency with which phosphorus is removed by lime is not as high as would be predicted by the low solubility of hydroxyapatite, $Ca_5OH(PO_4)_3$. Some of the possible reasons for this are slow precipitation of $Ca_5OH(PO_4)_3$, formation of nonsettling colloids; precipitation of calcium as $CaCO_3$ in certain pH ranges, and the fact that phosphate may be present as condensed phosphates (polyphosphates), which form soluble complexes with calcium ion.

Phosphate can be removed from solution by adsorption on some solids, particularly activated alumina, Al_2O_3. Removals of up to 99.9% of orthophosphate have been achieved with this method.

Nitrogen Removal

Next to phosphorus, nitrogen is the algal nutrient most commonly removed as part of advanced wastewater treatment. The techniques most often used for nitrogen removal are summarized in Table 13.2. Nitrogen in municipal wastewater generally is present as organic nitrogen or ammonia. Ammonia is the primary nitrogen product produced by most biological waste treatment processes. This is because it is expensive to aerate sewage sufficiently to oxidize the ammonia to nitrate through the action of nitrifying bacteria. If the activated sludge process is operated under conditions such that the nitrogen is maintained in the form of ammonia, the latter may be stripped in the form of NH_3 gas from the water by air. For ammonia stripping to work, the ammoniacal nitrogen must be converted to volatile NH_3 gas, which requires a pH substantially higher than the pK_a of the NH_4^+ ion. In practice, the pH is raised to approximately 11.5 by the addition of lime (which also serves to remove phosphate). The ammonia is stripped from the water by air.

Nitrification followed by denitrification is arguably the most effective technique for the removal of nitrogen from wastewater. The first step is an essentially complete conversion of ammonia and organic nitrogen to nitrate under strongly aerobic conditions, achieved by more extensive than normal aeration of the sewage:

$$NH_4^+ + 2O_2 \text{ (Nitrifying bacteria)} \rightarrow NO_3^- + 2H^+ + H_2O \quad (13.9.5)$$

The second step is the reduction of nitrate to nitrogen gas. This reaction is also bacterially catalyzed and requires a carbon source and a reducing agent such as methanol, CH_3OH.[8]

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Table 13.2 Common Processes for the Removal of Nitrogen from Wastewater[1]

Process	Principles and conditions
Air stripping ammonia	Ammonium ion is the initial product of biodegradation of nitrogen waste. It is removed by raising the pH to approximately 11 with lime, and stripping ammonia gas from the water by air in a stripping tower. Scaling, icing, and air pollution are the main disadvantages.
Ammonium ion exchange	Clinoptilolite, a natural zeolite, selectively removes ammonium ion by ion exchange: $Na^+\{^-\text{clinoptilolite}\} + NH_4^+ \rightarrow NH_4^+\{^-\text{clinoptilolite}\} + Na^+$. The ion exchanger is regenerated with sodium or calcium salts.
Biosynthesis	The production of biomass in the sewage treatment system and its subsequent removal from the sewage effluent result in a net loss of nitrogen from the system.
Nitrification-denitrification	This approach involves the conversion of ammoniacal nitrogen to nitrate by bacteria under aerobic conditions, $2NH_4^+ + 3O_2 \xrightarrow{Nitrosomonas} 4H^+ + 2NO_2^- + 2H_2O$ $2NO_2^- + O_2 \xrightarrow{Nitrobacter} 2NO_3^-$ followed by production of elemental nitrogen (denitrification): $4NO_3^- + 5\{CH_2O\} + 4H^+ \xrightarrow[\text{bacteria}]{\text{Denitrifying}} 2N_2(g) + 5CO_2(g) + 7H_2O$ Typically, denitrification is carried out in an anaerobic column with added methanol as a food source (microbial reducing agent).
Chlorination	Reaction of ammonium ion and hypochlorite (from chlorine) results in denitrification by chemical reactions: $NH_4^+ + HOCl \rightarrow NH_2Cl + H_2O + H^+$ $2NH_2Cl + HOCl \rightarrow N_2(g) + 3H^+ + 3\,Cl^-\,H_2O$

$$6NO_3^- + 5CH_3OH + 6H^+ \text{ (Denitrifying bacteria)} \rightarrow 3N_2(g) + 5CO_2 + 13H_2O \qquad (13.9.6)$$

The denitrification process shown in Reaction 13.9.6 can be carried out either in a tank or on a carbon column. In pilot plant operation, conversions of 95% of the ammonia to nitrate and 86% of the nitrate to nitrogen have been achieved. Although methanol is shown in the reaction as a source of reducing agent for the microbial reduction of nitrate, other organic substances can be used as well. Ethanol from the fermentation of otherwise waste carbohydrates would serve as a reducing substance.

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13.10 SLUDGE

Perhaps the most pressing water treatment problem at this time has to do with sludge collected or produced during water treatment. Finding a safe place to put the sludge or a use for it has proven troublesome, and the problem is aggravated by the growing numbers of water treatment systems.

Some sludge is present in wastewater prior to treatment and can be collected from it. Such sludge includes human wastes, garbage grindings, organic wastes and inorganic silt and grit from storm water runoff, and organic and inorganic wastes from commercial and industrial sources. There are two major kinds of sludge generated in a waste treatment plant. The first of these is organic sludge from activated sludge, trickling filter, or rotating biological reactors. The second is inorganic sludge from the addition of chemicals, such as in phosphorus removal (see Section 13.9).

Most commonly, sewage sludge is subjected to anaerobic digestion in a digester designed to allow bacterial action to occur in the absence of air. This reduces the mass and volume of sludge and ideally results in the formation of a stabilized humus. Disease agents are also destroyed in the process.

Following digestion, sludge is generally conditioned and thickened to concentrate and stabilize it and make it more dewaterable. Relatively inexpensive processes, such as gravity thickening, may be employed to get the moisture content down to about 95%. Sludge can be further conditioned chemically by the addition of iron or aluminum salts, lime, or polymers.

Sludge dewatering is employed to convert the sludge from an essentially liquid material to a damp solid containing not more than about 85% water. This can be accomplished on sludge drying beds consisting of layers of sand and gravel. Mechanical devices can also be employed, including vacuum filtration, centrifugation, and filter presses. Heat can be used to aid the drying process.

Ultimately, disposal of the sludge is required.Two of the main alternatives for sludge disposal are land spreading and incineration.

Rich in nutrients, waste sewage sludge contains around 5% N, 3% P, and 0.5% K on a dry-weight basis and can be used to fertilize and condition soil. The humic material in the sludge improves the physical properties and cation-exchange capacity of the soil. Possible accumulation of heavy metals is of some concern insofar as the use of sludge on cropland is concerned. Sewage sludge is an efficient heavy-metals scavenger and may contain elevated levels of zinc, copper, nickel, and cadmium These and other metals tend to remain immobilized in soil by chelation with organic matter, adsorption on clay minerals, and precipitation as insoluble compounds such as oxides or carbonates. However, increased application of sludge on cropland has caused distinctly elevated levels of zinc and cadmium in both leaves and grain of corn. Therefore, caution has been advised in heavy or prolonged application of sewage sludge to soil. Prior control of heavy-metal contamination from industrial sources has greatly reduced the heavy-metal content of sludge and enabled it to be used more extensively on soil.

An increasing problem in sewage treatment arises from sludge sidestreams. These consist of water removed from sludge by various treatment processes. Sewage treatment processes can be divided into mainstream treatment processes (primary clarification, trickling filter, activated sludge, and rotating biological reactor) and

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sidestream processes. During sidestream treatment, sludge is dewatered, degraded, and disinfected by a variety of processes, including gravity thickening, dissolved air flotation, anaerobic digestion, aerobic digestion, vacuum filtration, centrifugation, belt-filter press filtration, sand-drying-bed treatment, sludge-lagoon settling, wet air oxidation, pressure filtration, and Purifax treatment. Each of these produces a liquid byproduct sidestream that is circulated back to the mainstream. These add to the biochemical oxygen demand and suspended solids of the mainstream.

A variety of chemical sludges are produced by various water treatment and industrial processes. Among the most abundant of such sludges is alum sludge produced by the hydrolysis of Al(III) salts used in the treatment of water, which creates gelatinous aluminum hydroxide:

$$Al^{3+} + 3OH^{-}(aq) \rightarrow Al(OH)_3(s) \qquad (13.10.1)$$

Alum sludges normally are 98% or more water and are very difficult to dewater.

Both iron(II) and iron(III) compounds are used for the removal of impurities from wastewater by precipitation of $Fe(OH)_3$. The sludge contains $Fe(OH)_3$ in the form of soft, fluffy precipitates that are difficult to dewater beyond 10 or 12% solids.

The addition of either lime, $Ca(OH)_2$, or quicklime, CaO, to water is used to raise the pH to about 11.5 and cause the precipitation of $CaCO_3$, along with metal hydroxides and phosphates. Calcium carbonate is readily recovered from lime sludges and can be recalcined to produce CaO, which can be recycled through the system.

Metal hydroxide sludges are produced in the removal of metals such as lead, chromium, nickel, and zinc from wastewater by raising the pH to such a level that the corresponding hydroxides or hydrated metal oxides are precipitated. The disposal of these sludges is a substantial problem because of their toxic heavy-metal content. Reclamation of the metals is an attractive alternative for these sludges.

Pathogenic (disease-causing) microorganisms may persist in the sludge left from the treatment of sewage. Many of these organisms present potential health hazards, and there is risk of public exposure when the sludge is applied to soil. Therefore, it is necessary both to be aware of pathogenic microorganisms in municipal wastewater treatment sludge and to find a means of reducing the hazards caused by their presence.

The most significant organisms in municipal sewage sludge include (1) indicators of fecal pollution, including fecal and total coliform; (2) pathogenic bacteria, including *Salmonellae* and *Shigellae*; (3) enteric (intestinal) viruses, including enterovirus and poliovirus; and (4) parasites, such as *Entamoeba histolytica* and *Ascaris lumbricoides*.

Several methods are recommended to significantly reduce levels of pathogens in sewage sludge. Aerobic digestion involves aerobic agitation of the sludge for periods of 40 to 60 days (longer times are employed with low sludge temperatures). Air drying involves draining and/or drying of the liquid sludge for at least 3 months in a layer 20–25 cm thick. This operation can be performed on underdrained sand beds or in basins. Anaerobic digestion involves maintenance of the sludge in an anaerobic state for periods of time ranging from 60 days at 20˚C to 15 days at temperatures exceeding 35˚C. Composting involves mixing dewatered sludge cake with bulking

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agents subject to decay, such as wood chips or shredded municipal refuse, and allowing the action of bacteria to promote decay at temperatures ranging up to 45–65˚C. The higher temperatures tend to kill pathogenic bacteria. Finally, pathogenic organisms can be destroyed by lime stabilization in which sufficient lime is added to raise the pH of the sludge to 12 or higher.

13.11 WATER DISINFECTION

Chlorine is the most commonly used disinfectant employed for killing bacteria in water. When chlorine is added to water, it rapidly hydrolyzes according to the reaction

$$Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl \quad (13.11.1)$$

which has the following equilibrium constant:

$$K = \frac{[H^+][Cl^-][HOCl]}{[Cl_2]} = 4.5 \times 10^{-4} \quad (13.11.2)$$

Hypochlorous acid, HOCl, is a weak acid that dissociates according to the reaction,

$$HOCl \leftarrow \rightarrow H^+ + OCl^- \quad (13.11.3)$$

with an ionization constant of 2.7×10^{-8}. From the above it can be calculated that the concentration of elemental Cl_2 is negligible at equilibrium above pH 3 when chlorine is added to water at levels below 1.0 g/L.

Sometimes, hypochlorite salts are substituted for chlorine gas as a disinfectant. Calcium hypochlorite, $Ca(OCl)_2$, is commonly used. The hypochlorites are safer to handle than gaseous chlorine.

The two chemical species formed by chlorine in water, HOCl and OCl^-, are known as **free available chlorine**. Free available chlorine is very effective in killing bacteria. In the presence of ammonia, monochloramine, dichloramine, and trichloramine are formed:

$$NH_4^+ + HOCl \rightarrow NH_2Cl \text{ (monochloramine)} + H_2O + H^+ \quad (13.11.4)$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 \text{ (dichloramine)} + H_2O \quad (13.11.5)$$

$$NHCl_2 + HOCl \rightarrow NCl_3 \text{ (trichloramine)} + H_2O \quad (13.11.6)$$

The chloramines are called **combined available chlorine**. Chlorination practice frequently provides for formation of combined available chlorine which, although a weaker disinfectant than free available chlorine, is more readily retained as a disinfectant throughout the water distribution system. Too much ammonia in water is considered undesirable because it exerts excess demand for chlorine.

At sufficiently high Cl:N molar ratios in water containing ammonia, some HOCl and OCl^- remain unreacted in solution, and a small quantity of NCl_3 is formed. The ratio at which this occurs is called the **breakpoint**. Chlorination beyond the break-

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point ensures disinfection. It has the additional advantage of destroying the more common materials that cause odor and taste in water.

At moderate levels of NH_3-N (approximately 20 mg/L), when the pH is between 5.0 and 8.0, chlorination with a minimum 8:1 weight ratio of Cl to NH_3-nitrogen produces efficient denitrification:

$$NH_4^+ + HOCl \rightarrow NH_2Cl + H_2O + H^+ \quad (13.11.4)$$

$$2NH_2Cl + HOCl \rightarrow N_2(g) + 3H^+ + 3Cl^- + H_2O \quad (13.11.7)$$

This reaction is used to remove pollutant ammonia from wastewater. However, problems can arise from chlorination of organic wastes. Typical of such by-products is chloroform, produced by the chlorination of humic substances in water.

Chlorine is used to treat water other than drinking water. It is employed to disinfect effluent from sewage treatment plants, as an additive to the water in electric power plant cooling towers, and to control microorganisms in food processing.

Chlorine Dioxide

Chlorine dioxide, ClO_2, is an effective water disinfectant that is of particular interest because, in the absence of impurity Cl_2, it does not produce impurity trihalomethanes in water treatment. In acidic and neutral water, respectively, the two half-reactions for ClO_2 acting as an oxidant are the following:

$$ClO_2 + 4H^+ + 5e^- \leftarrow \rightarrow Cl^- + 2H_2O \quad (13.11.8)$$

$$ClO_2 + e^- \leftarrow \rightarrow ClO_2^- \quad (13.11.9)$$

In the neutral pH range, chlorine dioxide in water remains largely as molecular ClO_2 until it contacts a reducing agent with which to react. Chlorine dioxide is a gas that is violently reactive with organic matter and explosive when exposed to light. For these reasons, it is not shipped, but is generated on-site by processes such as the reaction of chlorine gas with solid sodium hypochlorite:

$$2NaClO_2(s) + Cl_2(g) \leftarrow \rightarrow 2ClO_2(g) + 2NaCl(s) \quad (13.11.10)$$

A high content of elemental chlorine in the product may require its purification to prevent unwanted side-reactions from Cl_2.

As a water disinfectant, chlorine dioxide does not chlorinate or oxidize ammonia or other nitrogen-containing compounds. Some concern has been raised over possible health effects of its main degradation byproducts, ClO_2^- and ClO_3^-.

Ozone

Ozone is sometimes used as a disinfectant in place of chlorine, particularly in Europe. Figure 13.l0 shows the main components of an ozone water treatment system. Basically, air is filtered, cooled, dried, and pressurized, then subjected to an electrical discharge of approximately 20,000 volts. The ozone produced is then pumped into a contact chamber, where water contacts the ozone for 10–15 minutes.

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Concern over possible production of toxic organochlorine compounds by water chlorination processes has increased interest in ozonation. Furthermore, ozone is more destructive to viruses than is chlorine. Unfortunately, the solubility of ozone in water is relatively low, which limits its disinfective power.

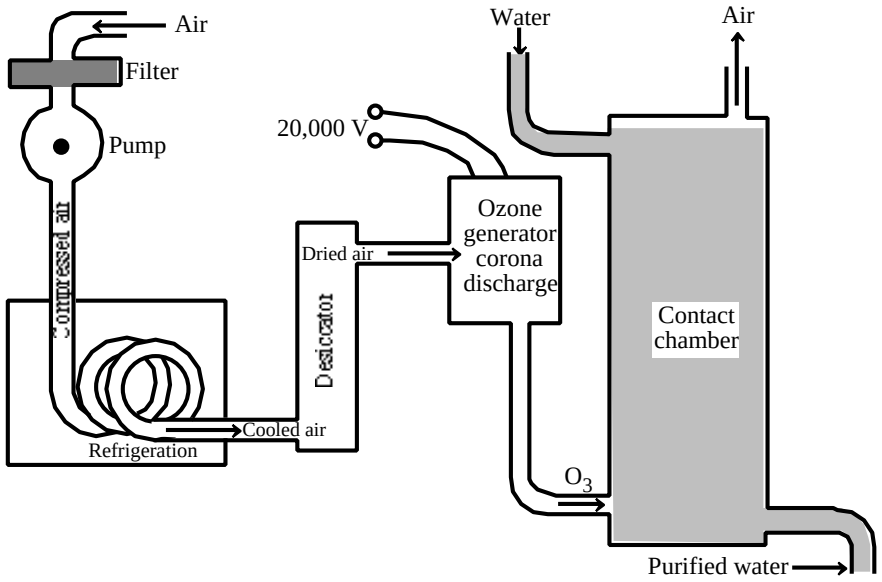


Figure 13.10 A schematic diagram of a typical ozone water-treatment system.

A major consideration with ozone is the rate at which it decomposes spontaneously in water, according to the overall reaction,

$$2O_3 \rightarrow 3O_2(g) \qquad (13.11.11)$$

Because of the decomposition of ozone in water, some chlorine must be added to maintain disinfectant throughout the water distribution system.

Iron(VI) in the form of ferrate ion, FeO_4^{2-}, is a strong oxidizing agent with excellent disinfectant properties. It has the additional advantage of removing heavy metals, viruses, and phosphate. It may well find limited application for disinfection in the future.

13.12 NATURAL WATER PURIFICATION PROCESSES

Virtually all of the materials that waste-treatment processes are designed to eliminate can be absorbed by soil or degraded in soil. In fact, most of these materials can serve to add fertility to soil. Wastewater can provide the water that is essential to plant growth. The mineralization of biological wastes in wastewater provides phosphorus, nitrogen and potassium usually provided by fertilizers. Wastewater also contains essential trace elements and vitamins. Stretching the point a bit, the degradation of organic wastes provides the CO_2 essential for photosynthetic production of plant biomass.

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Soil may be viewed as a natural filter for wastes. Most organic matter is readily degraded in soil and, in principle, soil constitutes an excellent primary, secondary, and tertiary treatment system for water. Soil has physical, chemical, and biological characteristics that can enable wastewater detoxification, biodegradation, chemical decomposition, and physical and chemical fixation. A number of soil characteristics are important in determining its use for land treatment of wastes. These characteristics include physical form, ability to retain water, aeration, organic content, acid-base characteristics, and oxidation-reduction behavior. Soil is a natural medium for a number of living organisms that may can an effect upon biodegradation of wastewaters, including those that contain industrial wastes. Of these, the most important are bacteria, including those from the genera *Agrobacterium*, *Arthrobacteri*, *Bacillus*, *Flavobacterium,* and *Pseudomonas.* Actinomycetes and fungi are important in decay of vegetable matter and may be involved in biodegradation of wastes. Other unicellular organisms that may be present in or on soil are protozoa and algae. Soil animals, such as earthworms, affect soil parameters such as soil texture. The growth of plants in soil may have an influence on its waste treatment potential in such aspects as uptake of soluble wastes and erosion control.

Early civilizations, such as the Chinese, used human organic wastes to increase soil fertility, and the practice continues today. The ability of soil to purify water was noted well over a century ago. In 1850 and 1852, J. Thomas Way, a consulting chemist to the Royal Agricultural Society in England, presented two papers to the Society entitled “Power of Soils to Absorb Manure.” Mr. Way’s experiments showed that soil is an ion exchanger. Much practical and theoretical information on the ion exchange process resulted from his work.

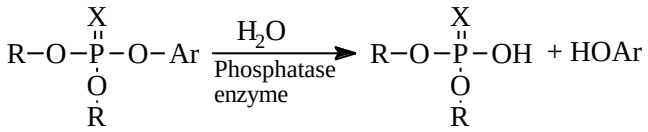
If soil treatment systems are not properly designed and operated, odor can become an overpowering problem. The author of this book is reminded of driving into a small town, recalled from some years before as a very pleasant place, and being assaulted with a virtually intolerable odor. The disgruntled residents pointed to a large spray irrigation system on a field in the distance—unfortunately upwind—spraying liquified pig manure as part of an experimental feedlot waste treatment operation. The experiment was not deemed a success and was discontinued by the investigators, presumably before they met with violence from the local residents.

Industrial Wastewater Treatment by Soil

Wastes that are amenable to land treatment are biodegradable organic substances, particularly those contained in municipal sewage and in wastewater from some industrial operations, such as food processing. However, through acclimation over a long period of time, soil bacterial cultures may develop that are effective in degrading normally recalcitrant compounds that occur in industrial wastewater. Acclimated microorganisms are found particularly at contaminated sites, such as those where soil has been exposed to crude oil for many years.

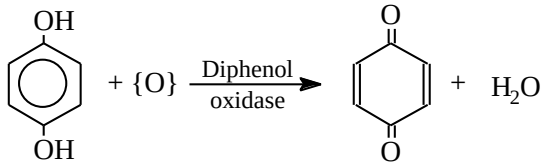
A variety of enzyme activities are exhibited by microorganisms in soil that enable them to degrade synthetic substances. Even sterilized soil may show enzyme activity due to extracellular enzymes secreted by microorganisms in soil. Some of these enzymes are hydrolase enzymes (see Chapter 21), such as those that catalyze the hydrolysis of organophosphate compounds as shown by the reaction,

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(13.12.1)

where R is an alkyl group, Ar is a substituent group that is frequently aryl, and X is either S or O. Another example of a reaction catalyzed by soil enzymes is the oxidation of phenolic compounds by diphenol oxidase:



(13.12.2)

Land treatment is most used for petroleum-refining wastes and is applicable to the treatment of fuels and wastes from leaking underground storage tanks. It can also be applied to biodegradable organic chemical wastes, including some organohalide compounds. Land treatment is not suitable for the treatment of wastes containing acids, bases, toxic inorganic compounds, salts, heavy metals, and organic compounds that are excessively soluble, volatile, or flammable.

13.13 WATER REUSE AND RECYCLING

Water reuse and recycling are becoming much more common as demands for water exceed supply. **Unplanned reuse** occurs as the result of waste effluents entering receiving waters or groundwater and subsequently being taken into a water distribution system. A typical example of unplanned water reuse occurs in London, which withdraws water from the Thames River that may have been through other water systems at least once, and which uses groundwater sources unintentionally recharged with sewage effluents from a number of municipalities. **Planned reuse** utilizes wastewater treatment systems deliberately designed to bring water up to standards required for subsequent applications. The term **direct reuse** refers to water that has retained its identity from a previous application; reuse of water that has lost its identity is termed **indirect reuse**. The distinction also needs to be made between recycling and reuse. **Recycling** occurs internally before water is ever discharged. An example is condensation of steam in a steam power plant followed by return of the steam to boilers. **Reuse** occurs, for example, when water discharged by one user is taken as a water source by another user.

Reuse of water continues to grow because of two major factors. The first of these is lack of supply of water. The second is that widespread deployment of modern water treatment processes significantly enhances the quality of water available for reuse. These two factors come into play in semi-arid regions in countries with advanced technological bases. For example, Israel, which is dependent upon irrigation for essentially all its agriculture, reuses about 2/3 of the country's sewage effluent for irrigation, whereas the U.S., where water is relatively more available, uses only about 2–3% of its water for this purpose.

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Since drinking water and water used for food processing require the highest quality of all large applications, intentional reuse for potable water is relatively less desirable, though widely practiced unintentionally or out of necessity. This leaves three applications with the greatest potential for reuse:

- Irrigation for cropland, golf courses, and other applications requiring water for plant and grass growth. This is the largest potential application for reused water and one that can take advantage of plant nutrients, particularly nitrogen and phosphorus, in water.
- Cooling and process water in industrial applications. For some industrial applications, relatively low-quality water can be used and secondary sewage effluent is a suitable source.
- Groundwater recharge. Groundwater can be recharged with reused water either by direct injection into an aquifer or by applying the water to land, followed by percolation into the aquifer. The latter, especially, takes advantage of biodegradation and chemical sorption processes to further purify the water.

It is inevitable that water recycling and reuse will continue to grow. This trend will increase the demand for water treatment, both qualitatively and quantitatively. In addition, it will require more careful consideration of the original uses of water to minimize water deterioration and enhance its suitability for reuse.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

The major categories for water treatment are [1]_____ _____ _____. Sources of water treated for municipal use include [2]_____. External treatment of water for industrial use is usually applied to [3]_____ _____ whereas internal treatment is designed to [4]_____ _____. Removal of [5]_____ _____ is essential for the treatment of boiler feedwater. [6]_____ _____ must be removed from water used in food processing. Current processes for the treatment of wastewater (sewage) may be divided into the three main categories of [7]_____ _____. Primary treatment of water is designed to remove [8]_____. The major constituent removed from water by secondary wastewater treatment is [9]_____ _____. Generally regarded as the most versatile and effective means of secondary wastewater treatment, the [10]_____ process uses a [11]_____ in an aerated tank to remove

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BOD from water. The reaction by which sewage sludge may be digested in the absence of oxygen by methane-producing anaerobic bacteria is [12]_____ _____ and it reduces [13]_____ _____ by about 60%. Tertiary waste treatment normally is applied to [14]_____ _____, and the three general kinds of contaminants that it removes are [15]_____ _____. Five major operations in a physical-chemical wastewater treatment process are [16]_____ _____ _____. Two factors that have prevented development of physical-chemical wastewater treatment are [17]_____. Some physical processes used in industrial wastewater treatment are [18]_____ _____ _____. Before colloidal solids can be removed by filtration, they usually must be subjected to [19]_____. A reaction by which water becomes softened when heated is [20]_____ _____. The reaction by which water containing "bicarbonate hardness," can be treated by addition of lime is [21]_____. _____. When bicarbonate ion is not present at substantial levels, softening water by $CaCO_3$ removal requires [22]_____ _____. Two reactions involving a solid ion exchanger by which hardness may be removed from water are [23]_____ _____ _____. The basic method for removing both soluble iron and manganese from water is [24]_____ _____. The removal of mercury, cadmium, or lead by lime treatment is aided by addition of [25]_____. The standard method of removing organic compounds from water is [26]_____ _____. Some methods for removing dissolved inorganic material from water are [27]_____ _____. A water purification process that consists of forcing pure water through a semipermeable membrane that allows the passage of water but not of other material is [28]_____ _____. Phosphorus is removed in advanced wastewater treatment to [29]_____. Phosphorus removal is usually accomplished by addition of [30]_____ for which the reaction is [31]_____. At a very high aeration rate in an activated sludge treatment process, phosphate is commonly removed because [32]_____ _____. The two overall biological reactions by which nitrogen, originally present as NH_4^+, can be removed from water are [33]_____ _____ and [34]_____. Anaerobic digestion of sewage sludge in a digester serves to [35]_____ _____. major plant nutrients contained in

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sewage sludge are [36]_____ _____. Sludge created by the water treatment reacation $Al^{3+} + 3OH^{-}(s) \rightarrow Al(OH)_3(aq)$ is known as alum sludge and causes problems because it is [37]_____. The most significant classes of organisms in municipal sludge are [38]_____ _____ _____. The most commonly used water disinfectant is [39]_____ which reacts with water according to the reaction [40]_____. Free available chlorine consists of [41]_____ in water, and combined available chlorine consists of [42]_____. Chlorine dioxide is of particular interest for water disinfection because it does not produce [43]_____ _____. An oxidizing disinfectant that does not contain chlorine is [44]_____ produced by [45]_____. Soil has physical, chemical, and biological characteristics that can enable [46]_____ _____ _____ of impurities in wastewater. The soil characteristics that are important in determining its use for land treatment of wastes are [47]_____ _____ _____. Acclimated microorganisms adapted to degradation of organic compounds are found most commonly at [48]_____ _____.

Answers to Chapter Summary

1. purification for domestic use, treatment for specialized industrial applications, treatment of wastewater to make it acceptable for release or reuse
2. river water and well water
3. the plant's entire water supply
4. modify the properties of water for specific applications
5. corrosive substances and scale-forming solutes
6. Pathogens and toxic substances
7. primary treatment, secondary treatment, and tertiary treatment
8. insoluble matter such as grit, grease, and scum from water
9. biochemical oxygen demand
10. activated sludge
11. suspension of microorganisms
12. $2\{CH_2O\} \rightarrow CH_4 + CO_2$
13. both the volatile-matter content and the volume of the sludge
14. a variety of processes performed on the effluent from secondary waste treatment
15. suspended solids, dissolved organic compounds, and dissolved inorganic materials
16. removal of scum and solid objects, clarification, generally with addition of a coagulant, and frequently with the addition of other chemicals (such as lime for phosphorus removal), filtration to remove filterable solids, activated carbon adsorption, disinfection
17. high costs of chemicals and energy

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18. density separation, filtration, flotation, evaporation, distillation, reverse osmosis, hyperfiltration, ultrafiltration, solvent extraction, air stripping, or steam stripping
19. coagulation
20. $Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + CO_2(g) + H_2O$
21. $Ca^{2+} + 2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3(s) + 2H_2O$
22. a source of CO_3^{2-} at a relatively high enough pH
23. $H^{+-}\{Cat(s)\} + Na^+ + Cl^- \rightarrow Na^{+-}\{Cat(s)\} + H^+ + Cl^-$ and $OH^{-+}\{An(s)\} + H^+ + Cl^- \rightarrow Cl^{-+}\{An(s)\} + H_2O$
24. oxidation to higher insoluble oxidation states
25. sulfide
26. activated carbon sorption
27. distillation, electrodialysis, ion exchange, reverse osmosis, nanofiltration, ultrafiltration, microfiltration, and dialysis
28. reverse osmosis
29. reduce algal growth
30. lime
31. $5Ca(OH)_2 + 3HPO_4^{2-} \rightarrow Ca_5OH(PO_4)_3(s) + 3H_2O + 6OH^-$
32. the CO_2 is swept out, the pH rises, and reactions occur such as $5Ca^{2+} + 3HPO_4^{2-} + H_2O \rightarrow Ca_5OH(PO_4)_3(s) + 4H^+$
33. $NH_4^+ + 2O_2$ (Nitrifying bacteria) $\rightarrow NO_3^- + 2H^+ + H_2O$
34. $6NO_3^- + 5CH_3OH + 6H^+$ (Denitrifying bacteria) $\rightarrow 3N_2(g) + 5CO_2 + 13H_2O$
35. reduce the mass and volume of sludge and destroys disease agent
36. 5% N, 3% P, and 0.5% K on a dry-weight basis
37. very difficult to dewater
38. indicators of fecal pollution, pathogenic bacteria, enteric viruses, and parasites
39. Cl_2
40. $Cl_2 + H_2O \rightarrow H^+ + Cl^- + HOCl$
41. HOCl and OCl^-
42. the chloramines
43. trihalomethanes
44. ozone
45. an electrical discharge through dry air
46. detoxification, biodegradation, chemical decomposition, and physical and chemical fixation
47. physical form, ability to retain water, aeration, organic content, acid-base characteristics, and oxidation-reduction behavior
48. sites contaminated with the kinds of wastes degraded

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QUESTIONS AND PROBLEMS

1. During municipal water treatment, air is often mixed intimately with the water, that is, it is aerated. What kinds of undesirable contaminants would this procedure remove from water?
2. What is the purpose of the return sludge step in the activated sludge process?
3. What are the two processes by which the activated sludge process removes soluble carbonaceous material from sewage?
4. Why might hard water be desirable as a medium if phosphorus is to be removed by an activated sludge plant operated under conditions of high aeration?
5. How does reverse osmosis differ from a simple sieve separation or ultrafiltration process?
6. How many liters of methanol would be required daily to remove the nitrogen from a 200,000-L/day sewage treatment plant producing an effluent containing 50 mg/L of nitrogen? Assume that the nitrogen has been converted to NO_3^- in the plant. The denitrifying reaction is Reaction 13.9.6.

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7. Discuss some of the advantages of physical-chemical treatment of sewage as opposed to biological wastewater treatment. What are some disadvantages?

8. Why is recarbonation necessary when water is softened by the lime-soda process?

9. Assume that a waste contains 300 mg/L of biodegradable $\{CH_2O\}$ and is processed through a 200,000-L/day sewage-treatment plant that converts 40% of the waste to CO_2 and H_2O. Calculate the volume of air (at 25°, 1 atm) required for this conversion. Assume that the O_2 is transferred to the water with 20% efficiency.

10. If all of the $\{CH_2O\}$ in the plant described in Question 9 could be converted to methane by anaerobic digestion, how many liters of methane (STP) could be produced daily?

11. Assuming that aeration of water does not result in the precipitation of calcium carbonate, of the following, which one would not be removed by aeration: hydrogen sulfide, carbon dioxide, volatile odorous bacterial metabolites, alkalinity, iron?

12. In which of the following water supplies would moderately high water hardness be most detrimental: municipal water; irrigation water; boiler feedwater; drinking water (in regard to potential toxicity).

13. Which solute in water is commonly removed by the addition of sulfite or hydrazine?

14. A wastewater containing dissolved Cu^{2+} ion is to be treated to remove copper. Which of the following processes would *not* remove copper in an insoluble form; lime precipitation; cementation; treatment with NTA; ion exchange; reaction with metallic Fe.

15. Match each water contaminant in the left column with its preferred method of removal in the right column.

A. Mn^{2+}	1. Activated carbon
B. Ca^{2+} and HCO_3^-	2. Raise pH by addition of Na_2CO_3
C. Trihalomethane compounds	3. Addition of lime
D. Mg^{2+}	4. Oxidation

16. A cementation reaction employs iron to remove Cd^{2+} present at a level of 350 mg/L from a wastewater stream. Given that the atomic weight of Cd is 112.4 and that of Fe is 55.8, how many kg of Fe are consumed in removing all the Cd from 4.50×10^6 liters of water?

17. Consider municipal drinking water from two different kinds of sources, one a flowing, well-aerated stream with a heavy load of particulate matter, and the other an anaerobic groundwater. Describe possible differences in the water treatment strategies for these two sources of water.

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18. In treating water for industrial use, consideration is often given to "sequential use of the water." What is meant by this term? Give some plausible examples of sequential use of water.

19. Active biomass is used in the secondary treatment of municipal wastewater. Describe three ways of supporting a growth of the biomass, contacting it with wastewater, and exposing it to air.

20. Using appropriate chemical reactions for illustration, show how calcium present as the dissolved HCO_3^- salt in water is easier to remove than other forms of hardness, such as dissolved $CaCl_2$.

21. Suggest a source of microorganisms to use in a waste-treatment process. Where should an investigator look for microorganisms to use in such an application? What are some kinds of wastes for which soil is particularly unsuitable as a treatment medium?

22. An *increase* in which of the following *decreases* the rate of oxidation of iron(II) to iron(III) in water? [Fe(II)]; pH; $[H^+]$; $[O_2]$; $[OH^-]$.

23. Label each of the following as external treatment (ex) or internal treatment (in): () aeration, () addition of inhibitors to prevent corrosion () adjustment of pH (), filtration, () clarification () removal of dissolved oxygen by reaction with hydrazine or sulfite, () disinfection for food processing

24. Label each of the following as primary treatment (pr), secondary treatment (sec), or tertiary treatment (tert): screening, comminuting, () grit removal, () BOD removal, () activated carbon filtration removal of dissolved organic compounds, () removal of dissolved inorganic materials

25. Both activated-sludge waste treatment and natural processes in streams and bodies of water remove degradable material by biodegradation. Explain why activated-sludge treatment is so much more effective.

26. Of the following, the one that does not belong with the rest is () removal of scum and solid objects, () clarification, () filtration, () degradation with activated sludge, () activated carbon adsorption, () disinfection.

27. Explain why complete physical-chemical wastewater-treatment systems are better than biological systems in dealing with toxic substances and overloads.

28. What are the two major ways in which dissolved carbon (organic compounds) are removed from water in industrial wastewater treatment. How do these two approaches differ fundamentally?

29. What is the reaction for the hydrolysis of aluminum ion in water? How is this reaction used for water treatment?

30. Explain why coagulation is used with filtration.

31. What are two major problems that arise from the use of excessively hard water?

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32. Show with chemical reactions how the removal of bicarbonate hardness with lime results in a net removal of ions from solution, whereas removal of nonbicarbonate hardness does not.
33. What two purposes are served by adding CO_2 to water that has been subjected to lime-soda softening?
34. Why is cation exchange normally used without anion exchange for softening water?
35. Show with chemical reactions how oxidation is used to remove soluble iron and manganese from water.
36. Show with chemical reactions how lime treatment, sulfide treatment, and cementation are used to remove heavy metals from water.
37. How is activated carbon prepared? What are the chemical reactions involved? What is remarkable about the surface area of activated carbon?
38. How is the surface of the membrane employed involved in the process of reverse osmosis?
39. Describe with a chemical reaction how lime is used to remove phosphate from water. What are some other chemicals that can be used for phosphate removal?
40. Why is nitrification required as a preliminary step in removal of nitrogen from water by biological denitrification?
41. What are some possible beneficial uses for sewage sludge? What are some of its characteristics that may make such uses feasible?
42. Distinguish between free available chlorine and combined available chlorine in water disinfection.
43. Give one major advantage and one major disadvantage of using chlorine dioxide for water disinfection.
44. Give one major advantage and one major disadvantage of using ozone dioxide for water disinfection.
45. Discuss how soil may be viewed as a natural filter for wastes. How does soil aid waste treatment? How can waste treatment be of benefit to soil in some cases?

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Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

14 THE ATMOSPHERE AND ATMOSPHERIC CHEMISTRY

14.1 THE ATMOSPHERE AND ATMOSPHERIC CHEMISTRY

The **atmosphere** composes the thin layer of mixed gases covering Earth's surface. Exclusive of water, atmospheric air is 78.1% (by volume) nitrogen, 21.0% oxygen, 0.9% argon, and 0.03% carbon dioxide. Normally, air is 1–3% water vapor by volume. In addition, air contains a large variety of trace level gases at levels below 0.002%, including neon, helium, methane, krypton, nitrous oxide, hydrogen, xenon, sulfur dioxide, ozone, nitrogen dioxide, ammonia, and carbon monoxide.

The atmosphere is divided into several layers on the basis of temperature. Of these, the most significant are the troposphere, extending in altitude from the earth's surface to approximately 11 kilometers (km); and the stratosphere, from about 11 km to approximately 50 km. The temperature of the troposphere ranges from an average of 15˚C at sea level to an average of -56˚C at its upper boundary. The average temperature of the stratosphere increases from -56˚C at its boundary with the troposphere to –2˚C at its upper boundary. The reason for this increase is absorption of solar ultraviolet energy by ozone (O_3) in the stratosphere.

Various aspects of the environmental chemistry of the atmosphere are discussed in this chapter and the two that follow. The most significant feature of atmospheric chemistry is the occurrence of **photochemical reactions** resulting from the absorption by molecules of light photons, designated $h\nu$. (The energy, E, of a photon of visible or ultraviolet light is given by the equation $E = h\nu$, where h is Planck's constant and ν is the frequency of light, which is inversely proportional to its wavelength. Ultraviolet radiation has a higher frequency than visible light and is, therefore, more energetic and more likely to break chemical bonds in molecules that absorb it. See the discussion of electromagnetic radiation in Section 3.11.) One of the most significant photochemical reactions is the one responsible for the presence of ozone in the stratosphere (see above), which is initiated when O_2 absorbs highly energetic ultraviolet radiation in the stratosphere to form oxygen atoms, which react further to produce ozone, O_3.

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Gaseous Oxides in the Atmosphere

Oxides of carbon, sulfur, and nitrogen are important constituents of the atmosphere and are pollutants at higher levels. Of these, carbon dioxide, CO_2, is the most abundant. It is a natural atmospheric constituent, and it is required for plant growth. However, as discussed in Chapter 15, the level of carbon dioxide in the atmosphere, now at about 365 parts per million (ppm) by volume, is increasing by about 1 ppm per year, which may well cause general atmospheric warming, the "greenhouse effect," with potentially very serious consequences for the global atmosphere and for life on earth.

Hydrocarbons and Photochemical Smog

The most abundant hydrocarbon in the atmosphere is methane, CH_4, released from underground sources as natural gas and produced by the fermentation of organic matter. Methane is one of the least reactive atmospheric hydrocarbons and is produced by diffuse sources, so that its participation in the formation of pollutant photochemical reaction products is minimal. The most significant atmospheric pollutant hydrocarbons are the reactive ones produced as automobile exhaust emissions. In the presence of NO, under conditions of temperature inversion (see Chapter 16), low humidity, and sunlight, these hydrocarbons produce undesirable **photochemical smog**, manifested by the presence of visibility-obscuring particulate matter, oxidants such as ozone, and noxious organic species such as aldehydes.

Particulate Matter

Particles ranging from aggregates of a few molecules to pieces of dust readily visible to the naked eye are commonly found in the atmosphere (Chapter 15). Colloidal-sized particles in the atmosphere are called **aerosols**. Some atmospheric particles, such as sea salt formed by the evaporation of water from droplets of sea spray, are natural and even beneficial atmospheric constituents. Very small particles called **condensation nuclei** serve as bodies for atmospheric water vapor to condense upon and are essential for the formation of rain drops.

14.2 IMPORTANCE OF THE ATMOSPHERE

The atmosphere is a protective blanket that nurtures life on the Earth and protects it from the hostile environment of outer space. The atmosphere is the source of carbon dioxide for plant photosynthesis and of oxygen for respiration. It provides the nitrogen that nitrogen-fixing bacteria and ammonia-manufacturing plants use to produce chemically bound nitrogen, an essential component of life molecules. As a basic part of the hydrologic cycle (Figure 11.1) the atmosphere transports water from the oceans to land, thus acting as the condenser in a vast solar-powered still. Unfortunately, the atmosphere also has been used as a dumping ground for many pollutant materials—ranging from sulfur dioxide to refrigerant Freon—a practice that causes damage to vegetation and materials, shortens human life, and alters the characteristics of the atmosphere itself.

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In its essential role as a protective shield, the atmosphere absorbs most of the cosmic rays from outer space and protects organisms from their effects. It also absorbs most of the electromagnetic radiation from the sun, allowing transmission of significant amounts of radiation only in the regions of 300–2500 nm (near-ultraviolet, visible, and near-infrared radiation) and 0.01–40 m (radio waves). By absorbing electromagnetic radiation below 300 nm, the atmosphere filters out damaging ultraviolet radiation that would otherwise be very harmful to living organisms. Furthermore, because it reabsorbs much of the infrared radiation by which absorbed solar energy is re-emitted to space, the atmosphere stabilizes the earth's temperature, preventing the tremendous temperature extremes that occur on planets and moons lacking substantial atmospheres.

14.3 PHYSICAL CHARACTERISTICS OF THE ATMOSPHERE

Atmospheric science deals with the movement of air masses in the atmosphere, atmospheric heat balance, and atmospheric chemical composition and reactions. To understand atmospheric chemistry and air pollution, it is important to have an overall appreciation of the atmosphere, its composition, and physical characteristics as discussed in the first parts of this chapter.

Atmospheric Composition

Dry air within several kilometers of ground level consists of two **major components**

- Nitrogen, 78.08 % (by volume)
- Oxygen, 20.95 %

two **minor components**

- Argon, 0.934 %
- Carbon dioxide, 0.036 %

in addition to argon, four more **noble gases**,

- Neon, 1.818×10^{-3} %
- Helium, 5.24×10^{-4} %
- Krypton, 1.14×10^{-4} %
- Xenon, 8.7×10^{-6} %

and **trace gases**, as given in Table 14.1. Atmospheric air may contain 0.1–5% water by volume, with a normal range of 1–3%.

Variation of Pressure and Density with Altitude

As anyone who has exercised at high altitudes well knows, the density of the atmosphere decreases sharply with increasing altitude as a consequence of the gas laws and gravity. More than 99% of the total mass of the atmosphere is found within approximately 30 km (about 20 miles) of the earth's surface. Such an altitude is minuscule compared with the earth's diameter, so it is not an exaggeration to charac-

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terize the atmosphere as a "tissue-thin" protective layer. Although the total mass of the global atmosphere is huge, approximately 5.14×10^{15} metric tons, it is still only about one millionth of the earth's total mass.

Table 14.1 Atmospheric Trace Gases in Dry Air Near Ground Level

Gas or species	Volume percent[1]	Major sources	Process for removal from the atmosphere
CH_4	1.6×10^{-4}	Biogenic[2]	Photochemical[3]
CO	$\sim 1.2 \times 10^{-5}$	Photochemical, anthropogenic[4]	Photochemical
N_2O	3×10^{-5}	Biogenic	Photochemical
NO_x[5]	10^{-10}–10^{-6}	Photochemical, lightning, anthropogenic	Photochemical
HNO_3	10^{-9}–10^{-7}	Photochemical	Washed out by precipitation
NH_3	10^{-8}–10^{-7}	Biogenic	Photochemical, washed out by precipitation
H_2	5×10^{-5}	Biogenic, photochemical	Photochemical
H_2O_2	10^{-8}–10^{-6}	Photochemical	Washed out by precipitation
HO·[6]	10^{-13}–10^{-10}	Photochemical	Photochemical
HO_2·[6]	10^{-11}–10^{-9}	Photochemical	Photochemical
H_2CO	10^{-8}–10^{-7}	Photochemical	Photochemical
CS_2	10^{-9}–10^{-8}	Anthropogenic, biogenic	Photochemical
OCS	10^{-8}	Anthropogenic, biogenic, photochemical	Photochemical
SO_2	$\sim 2 \times 10^{-8}$	Anthropogenic, photochemical, volcanic	Photochemical
I_2	0-trace	—	—
CCl_2F_2[7]	2.8×10^{-5}	Anthropogenic	Photochemical
H_3CCCl_3[8]	$\sim 1 \times 10^{-8}$	Anthropogenic	Photochemical

[1] Levels in the absence of gross pollution
[2] From biological sources
[3] Reactions induced by the absorption of light energy as described later in this chapter and in Chapters 15–16
[4] Sources arising from human activities
[5] Sum of NO, NO_2, and NO_3, of which NO_3 is a major reactive species in the atmosphere at night
[6] Reactive free radical species with 1 unpaired electron; these are transient species whose concentrations become much lower at night
[7] A chlorofluorocarbon, Freon F-12
[8] Methyl chloroform

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The fact that atmospheric pressure decreases as an approximately exponential function of altitude largely determines the characteristics of the atmosphere. Figure 14.1 shows the variation of the pressure, P_h, as a function of altitude. This figure shows the extremes of pressure and temperature that occur in the atmosphere. The characteristics of the atmosphere vary widely with altitude, time (season), location (latitude), and even solar activity. At very high altitudes, normally reactive species such as atomic oxygen, O, persist for long periods of time. That occurs because the pressure is very low at these altitudes such that the distance traveled by a reactive species before it collides with a potential reactant—its **mean free path**—is quite high. A particle with a mean free path of 1×10^{-6} cm at sea level has a mean free path greater than 1×10^{6} cm at an altitude of 500 km, where the pressure is lower by many orders of magnitude.

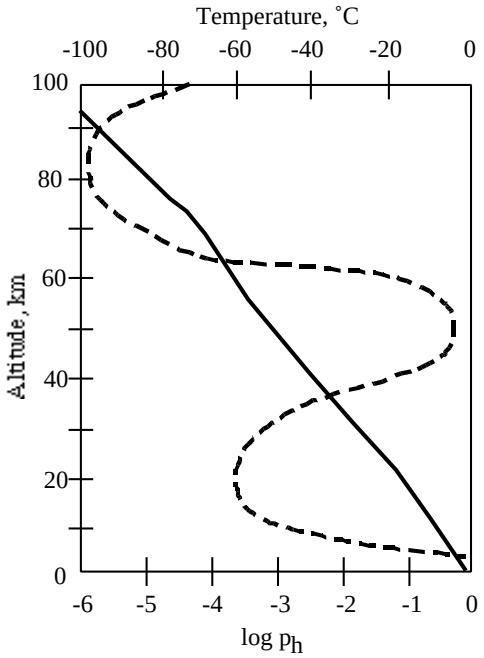


Figure 14.1 Variation of pressure (solid line) and temperature (dashed line) with altitude.

Stratification of the Atmosphere

As shown in Figure 14.2, the atmosphere is stratified on the basis of the temperature/density relationships resulting from interactions between physical and photochemical (light-induced chemical phenomena) processes in air.

The lowest layer of the atmosphere extending from sea level to an altitude of 10–16 km is the **troposphere**, characterized by a generally homogeneous composition of major gases other than water and decreasing temperature with increasing altitude from the heat-radiating surface of the earth. The upper limit of the troposphere, which has a temperature minimum of about -56˚C, varies in altitude by a kilometer or more with atmospheric temperature, underlying terrestrial surface, and

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time. The homogeneous composition of the troposphere results from constant mixing by circulating air masses. However, the water vapor content of the troposphere is extremely variable because of cloud formation, precipitation, and evaporation of water from terrestrial water bodies.

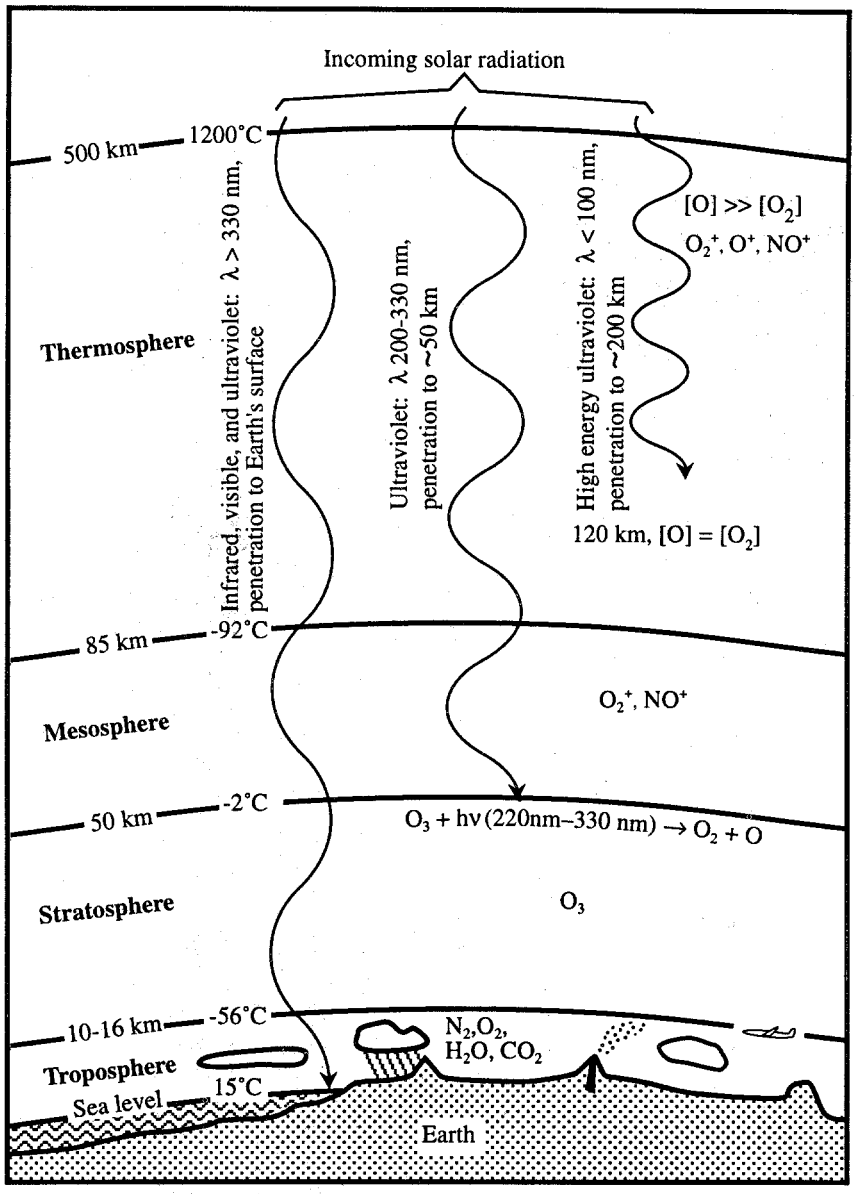


Figure 14.2 Major regions of the atmosphere (not to scale).

The very cold temperature of the **tropopause** layer at the top of the troposphere serves as a barrier that causes water vapor to condense to ice so that it cannot reach altitudes at which it would photodissociate through the action of intense high-energy

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ultraviolet radiation. If this happened, the hydrogen produced would escape the earth's atmosphere and be lost. (Much of the hydrogen and helium gases originally present in the earth's atmosphere were lost by this process.)

The atmospheric layer directly above the troposphere is the **stratosphere**, in which the temperature rises to a maximum of about -2˚C with increasing altitude. This phenomenon is due to the presence of ozone, O_3, which can reach a level of around 10 ppm by volume in the mid-range of the stratosphere. The heating effect is caused by the absorption of ultraviolet radiation energy by ozone, a phenomenon discussed later in this chapter.

The absence of high levels of radiation-absorbing species in the **mesosphere** immediately above the stratosphere results in a further temperature decrease to about -92˚C at an altitude around 85 km. The upper regions of the mesosphere and higher define a region, called the exosphere, from which molecules and ions can completely escape the atmosphere. Extending to the far outer reaches of the atmosphere is the **thermosphere**, in which the highly rarified gas reaches temperatures as high as 1200˚C by the absorption of very energetic radiation of wavelengths less than approximately 200 nm by gas species in this region.

14.4 ENERGY TRANSFER IN THE ATMOSPHERE

The physical and chemical characteristics of the atmosphere and the critical heat balance of the earth are determined by energy and mass transfer processes in the atmosphere. Energy transfer phenomena are addressed in this section and mass transfer in Section 14.5. Incoming solar energy is largely in the visible region of the spectrum. The shorter wavelength blue solar light is scattered relatively more strongly by molecules and particles in the upper atmosphere, which is why the sky is blue as it is viewed by scattered light. Similarly, light that has been transmitted through scattering atmospheres appears red, particularly around sunset and sunrise, and under circumstances in which the atmosphere contains a high level of particles. The solar energy flux reaching the atmosphere is huge, amounting to 1.34×10^3 watts per square meter (114.2 kcal per minute per square meter) perpendicular to the line of solar flux at the top of the atmosphere, as illustrated in Figure 14.3. This value is the **solar constant**, and may be termed **insolation**, which stands for "incoming solar radiation." If all this energy reached the earth's surface and was retained, the planet would have vaporized long ago. As it is, the complex factors involved in maintaining the Earth's heat balance within very narrow limits are crucial to retaining conditions of climate that will support present levels of life on earth. The great changes of climate that resulted in ice ages during some periods, or tropical conditions during others, were caused by variations of only a few degrees in average temperature. Marked climate changes within recorded history have been caused by much smaller average temperature changes. The mechanisms by which the earth's average temperature is retained within its present narrow range are complex and not completely understood, but the main features are explained here.

About half of the solar radiation entering the atmosphere reaches the earth's surface either directly or after scattering by clouds, atmospheric gases, or particles. The remaining half of the radiation is either reflected directly back or absorbed in the atmosphere, and its energy radiated back into space at a later time as infrared

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radiation. Most of the solar energy reaching the surface is absorbed and it must be returned to space to maintain heat balance. In addition, a very small amount of energy (less than 1% of that received from the sun) reaches the earth's surface by convection and conduction processes from the earth's hot mantle, and this, too, must be lost.

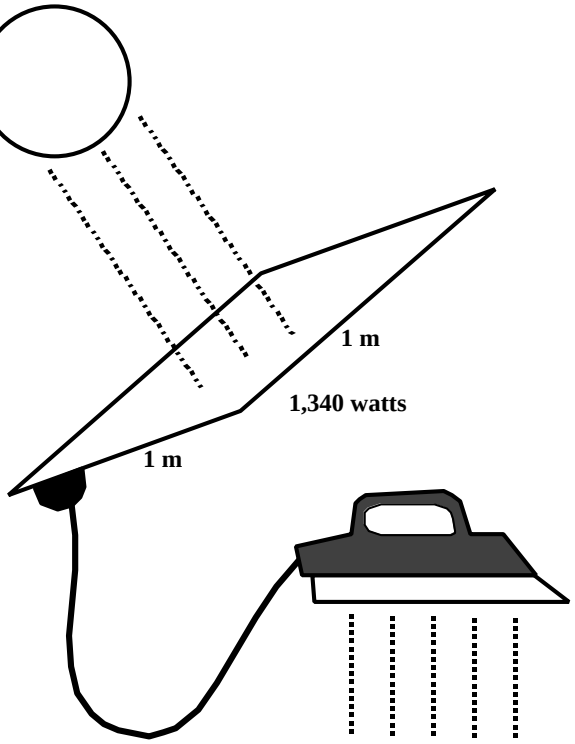


Figure 14.3 The solar flux at the distance of the earth from the sun is 1.34×10^3 watts/m^2.

Energy transport, which is crucial to eventual reradiation of energy from the earth, is accomplished by three major mechanisms. These are conduction, convection, and radiation. **Conduction** of energy occurs through the interaction of adjacent atoms or molecules without the bulk movement of matter and is a relatively slow means of transferring energy in the atmosphere. **Convection** involves the movement of whole masses of air, which may be either relatively warm or cold. It is the mechanism by which abrupt temperature variations occur when large masses of air move across an area. As well as carrying **sensible heat** due to the kinetic energy of molecules, convection carries **latent heat** in the form of water vapor that releases heat as it condenses. An appreciable fraction of the earth's surface heat is transported to clouds in the atmosphere by conduction and convection before being lost ultimately by radiation.

Radiation of energy in Earth's atmosphere occurs through electromagnetic radiation in the infrared region of the spectrum. Electromagnetic radiation is the only way in which energy is transmitted through a vacuum; therefore, it is the means by which all of the energy that must be lost from the planet to maintain its heat balance is ultimately returned to space. The electromagnetic radiation that carries energy

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away from the earth is of a much longer wavelength than the sunlight that brings energy to the earth. This is a crucial factor in maintaining the earth's heat balance, and one susceptible to upset by human activities. The maximum intensity of incoming radiation occurs at 0.5 micrometers (500 nanometers) in the visible region, with essentially none outside the range of 0.2 μm to 3 μm. This range encompasses the whole visible region and small parts of the ultraviolet and infrared adjacent to it. Outgoing radiation is in the infrared region, with maximum intensity at about 10 μm, primarily between 2 μm and 40 μm. Thus the earth loses energy by electromagnetic radiation of a much longer wavelength (lower energy per photon) than the radiation by which it receives energy.

Earth's Radiation Budget

The earth's radiation budget is illustrated in Figure 14.4. The average surface temperature is maintained at a relatively comfortable 15˚C because of an atmospheric "greenhouse effect" in which water vapor and, to a lesser extent, carbon dioxide reabsorb much of the outgoing radiation and reradiate about half of it back to the surface. Were this not the case, the surface temperature would be significantly lower, around -18˚C. Most of the absorption of infrared radiation is done by water molecules in the atmosphere. Absorption is weak in the regions 7–8.5 μm and 11–14 μm, and nonexistent between 8.5 μm and 11 μm, leaving a "hole" in the infrared absorption spectrum through which radiation may escape. Carbon dioxide, though present at a much lower concentration than water vapor, absorbs strongly between 12 μm and 16.3 μm, and plays a key role in maintaining the heat balance. There is concern that an increase in the carbon dioxide level in the atmosphere could prevent sufficient energy loss to cause a perceptible and damaging increase in the earth's temperature. This phenomenon, discussed in more detail in Section 15.6, is popularly known as the **greenhouse effect** and may occur from elevated CO_2 levels caused by increased use of fossil fuels and the destruction of massive quantities of forests.

An important aspect of solar radiation that reaches Earth's surface is the percentage reflected from the surface, described as **albedo**. Albedo is important in determining Earth's heat balance, in that absorbed radiation heats the surface, and reflected radiation does not. Albedo varies spectacularly with the surface. At the two extremes, freshly fallen snow has an albedo of 90% because it reflects 9/10 of incoming radiation, whereas freshly plowed black topsoil has an albedo of only about 2.5%.

14.5 ATMOSPHERIC MASS TRANSFER, METEOROLOGY, AND WEATHER

Meteorology is the science of atmospheric phenomena, encompassing the study of the movement of air masses as well as physical forces in the atmosphere—heat, wind, and transitions of water, primarily liquid to vapor or vice versa. Meteorological phenomena affect, and in turn are affected by, the chemical properties of the atmosphere. For example, before modern emission controls took effect, meteorological phenomena determined whether power plant stack gas heavily laced with

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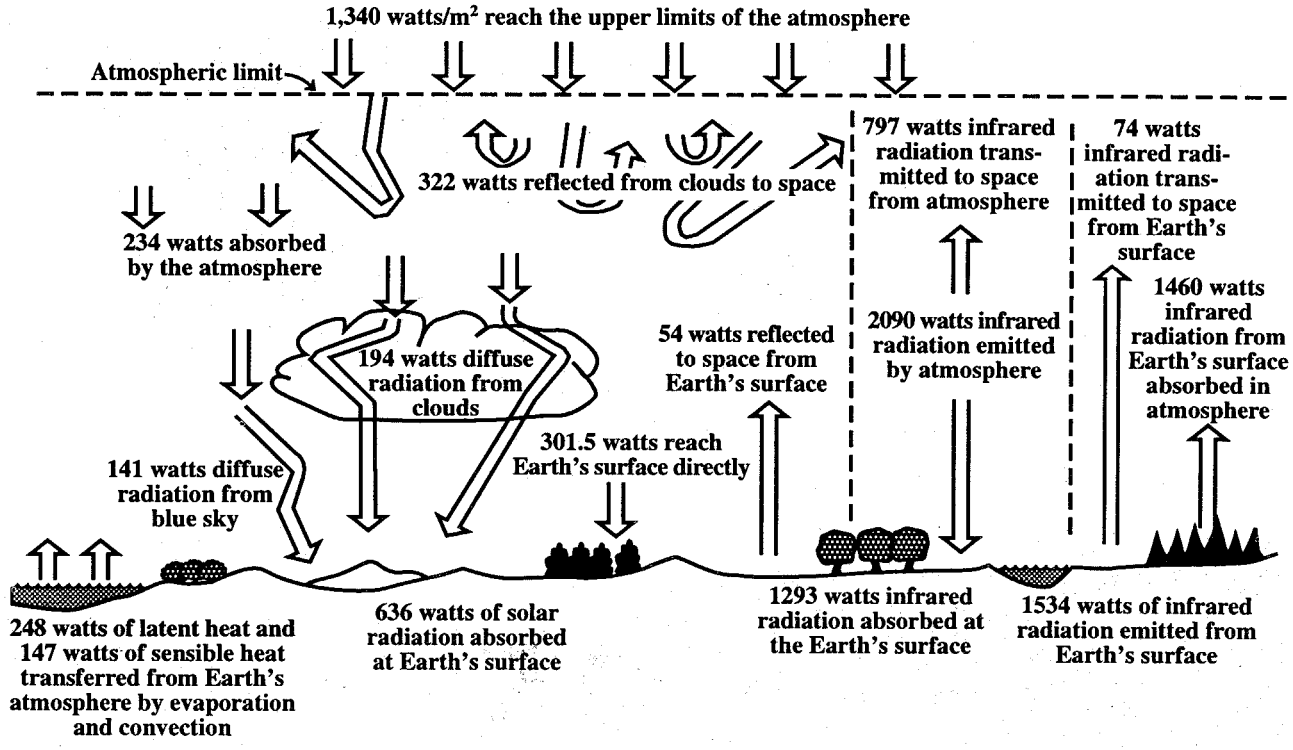


Figure 14.4. Earth's radiation budget expressed on the basis of portions of the 1340 watts/m² composing the solar flux.

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fur dioxide would be dispersed high in the atmosphere with little direct effect upon human health, or would settle as a choking chemical blanket in the vicinity of the power plant. Los Angeles largely owes its susceptibility to smog to the meteorology of the Los Angeles basin, which holds hydrocarbons and nitrogen oxides long enough to cook up an unpleasant brew of damaging chemicals under the intense rays of the sun (see the discussion of photochemical smog in Chapter 16). Short-term variations in the state of the atmosphere constitute **weather**. The weather is defined in terms of seven major factors: temperature, clouds, winds, humidity, horizontal visibility (as affected by fog, etc.), type and quantity of precipitation, and atmospheric pressure. All of these factors are closely interrelated. Longer-term variations and trends within a particular geographical region in those factors that compose weather are described as **climate**, a term defined and discussed in Section 14.7.

Atmospheric Water in Energy and Mass Transfer

The driving force behind weather and climate is the distribution and ultimate reradiation to space of solar energy. A large fraction of solar energy is converted to latent heat by evaporation of water into the atmosphere. As water condenses from atmospheric air, large quantities of heat are released. This is a particularly significant means for transferring energy from the ocean to land. Solar energy falling on the ocean is converted to latent heat by the evaporation of water, then the water vapor moves inland, where it condenses. The latent heat released when the water condenses warms the surrounding land mass.

Atmospheric water can be present as vapor, liquid, or ice. The water vapor content of air can be expressed as **humidity**. **Relative humidity**, expressed as a percentage, describes the amount of water vapor in the air as a ratio of the maximum amount that the air can hold at that temperature. Air with a given relative humidity can undergo any of several processes to reach the saturation point at which water vapor condenses in the form of rain or snow. For this condensation to happen, air must be cooled below a temperature called the **dew point**, and **condensation nuclei** must be present. These nuclei are hygroscopic substances such as salts, sulfuric acid droplets, and some organic materials, including bacterial cells. Air pollution in some forms is an important source of condensation nuclei.

The liquid water in the atmosphere is present largely in **clouds**. Clouds normally form when rising, adiabatically cooling air can no longer hold water in the vapor form, and the water forms very small aerosol droplets. Clouds can be classified in three major forms. Cirrus clouds occur at great altitudes and have a thin feathery appearance. Cumulus clouds are detached masses with a flat base and frequently a "bumpy" upper structure. Stratus clouds occur in large sheets and may cover all of the sky visible from a given point as overcast. Clouds are important absorbers and reflectors of radiation (heat). Their formation is affected by the products of human activities, especially particulate matter pollution and emission of deliquescent gases such as SO_2 and HCl.

The formation of precipitation from the very small droplets of water that compose clouds is a complicated and important process. Cloud droplets normally take somewhat longer than a minute to form by condensation. They average about

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0.04 mm across and do not exceed 0.2 mm in diameter. Raindrops range from 0.5–4 mm in diameter. Condensation processes do not form particles large enough to fall as precipitation (rain, snow, sleet, or hail). The small condensation droplets must collide and coalesce to form precipitation-size particles. When droplets reach a threshold diameter of about 0.04 mm, they grow more rapidly by coalescence with other particles than by condensation of water vapor.

Air Masses

Distinct air masses are a major feature of the troposphere. These air masses are uniform and horizontally homogeneous with respect to temperature and water vapor content. These characteristics are determined by the nature of the surface over which a large air mass forms. Polar continental air masses form over cold land regions; polar maritime air masses form over polar oceans. Air masses originating in the tropics may be similarly classified as tropical continental air masses or tropical maritime air masses. The movement of air masses and the conditions in them may have important effects upon pollutant reactions, effects, and dispersal.

Solar energy received by Earth is largely redistributed by the movement of huge masses of air with different pressures, temperatures, and moisture contents separated by boundaries called **fronts**. Horizontally moving air is called **wind**, whereas vertically moving air is referred to as an **air current**. Atmospheric air moves constantly, with behavior and effects that reflect the laws governing the behavior of gases. First of all, gases will move horizontally and/or vertically from regions of *high atmospheric pressure* to those of *low atmospheric pressure.* Furthermore, expansion of gases causes cooling, whereas compression causes warming. A mass of warm air tends to move from Earth's surface to higher altitudes, where the pressure is lower; in so doing, it expands *adiabatically* (that is, without exchanging energy with its surroundings) and becomes cooler. If there is no condensation of moisture from the air, the cooling effect is about 10˚C per 1000 meters of altitude, a figure known as the **dry adiabatic lapse rate**. A cold mass of air at a higher altitude does the opposite; it sinks and becomes warmer at about 10˚C/1000 m. Often, however, when there is sufficient moisture in rising air, water condenses from it, releasing latent heat. This partially counteracts the cooling effect of the expanding air, giving a **moist adiabatic lapse rate** of about 6˚C/1000 m. Parcels of air do not rise and fall, or even move horizontally in a completely uniform way, but exhibit eddies, currents, and various degrees of turbulence.

Wind—air moving horizontally—occurs because of differences in air pressure from high pressure regions to low pressure areas. Air currents (vertically moving air) are largely **convection currents** formed by differential heating of air masses. Air that is over a solar heated land mass is warmed, becomes less dense, and rises, to be replaced by cooler and more dense air. Wind and air currents are strongly involved with air pollution phenomena. Wind carries and disperses air pollutants. In some cases, the absence of wind can enable pollutants to collect in a region and undergo processes that lead to even more (secondary) pollutants. Prevailing wind direction is an important factor in determining the areas most affected by an air pollution source. Wind is an important renewable energy resource (see Chapter 24). Furthermore, wind plays an important role in the propagation of life by dispersing spores, seeds, and organisms, such as spiders.

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Topographical Effects

Topography, the surface configuration and relief features of the earth's surface, may strongly affect winds and air currents. Differential heating and cooling of land surfaces and bodies of water can result in **local convective winds**, including land breezes and sea breezes at different times of the day along the seashore, as well as breezes associated with large bodies of water inland. Mountain topography causes complex and variable localized winds. The masses of air in mountain valleys heat up during the day causing upslope winds, and cool off at night, causing downslope winds. Upslope winds flow over ridge tops in mountainous regions. The blocking of wind and of masses of air by mountain formations some distance inland from seashores can trap bodies of air, particularly when temperature inversion conditions occur (see Section 14.6).

Movement of Air Masses

Basically, weather is the result of the interactive effects of (1) redistribution of solar energy, (2) horizontal and vertical movement of air masses with varying moisture contents, and (3) evaporation and condensation of water, accompanied by uptake and release of heat. To see how these factors determine weather—and ultimately climate—on a global scale, first consider the cycle illustrated in Figure 14.5. This figure shows solar energy being absorbed by a body of water and causing some water to evaporate. The warm, moist mass of air thus produced moves from a region of high pressure to one of low pressure, and cools by expansion as it rises in what is called a **convection column**. As the air cools, water condenses from it and energy is released; this is a major pathway by which energy is transferred from the earth's surface to high in the atmosphere. As a result of condensation of water and loss of energy, the air is converted from warm, moist air to cool, dry air. Furthermore, the movement of the parcel of air to high altitudes results in a degree of "crowding" of air molecules and creates a zone of relatively greater pressure high in the troposphere at the top of the convection column. This air mass, in turn, moves from the upper-level region of high pressure to one of low pressure; in so doing, it subsides, thus creating an upper-level low pressure zone, and becomes warm, dry air in the process. The pileup of this air at the surface creates a surface high pressure zone where the cycle described above began. The warm, dry air in this surface high pressure zone again picks up moisture, and the cycle begins again.

Global Weather

The factors discussed above that determine and describe the movement of air masses are involved in the massive movement of air, moisture, and energy that occurs globally. The central feature of global weather is the redistribution of solar energy that falls unequally on earth at different latitudes (relative distances from the equator and poles). Consider Figure 14.6. Sunlight, and the energy flux from it, is most intense at the equator because, averaged over the seasons, solar radiation comes in perpendicular to Earth's surface at the equator. With increasing distance from the

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equator (higher latitudes) the angle is increasingly oblique and more of the energy-

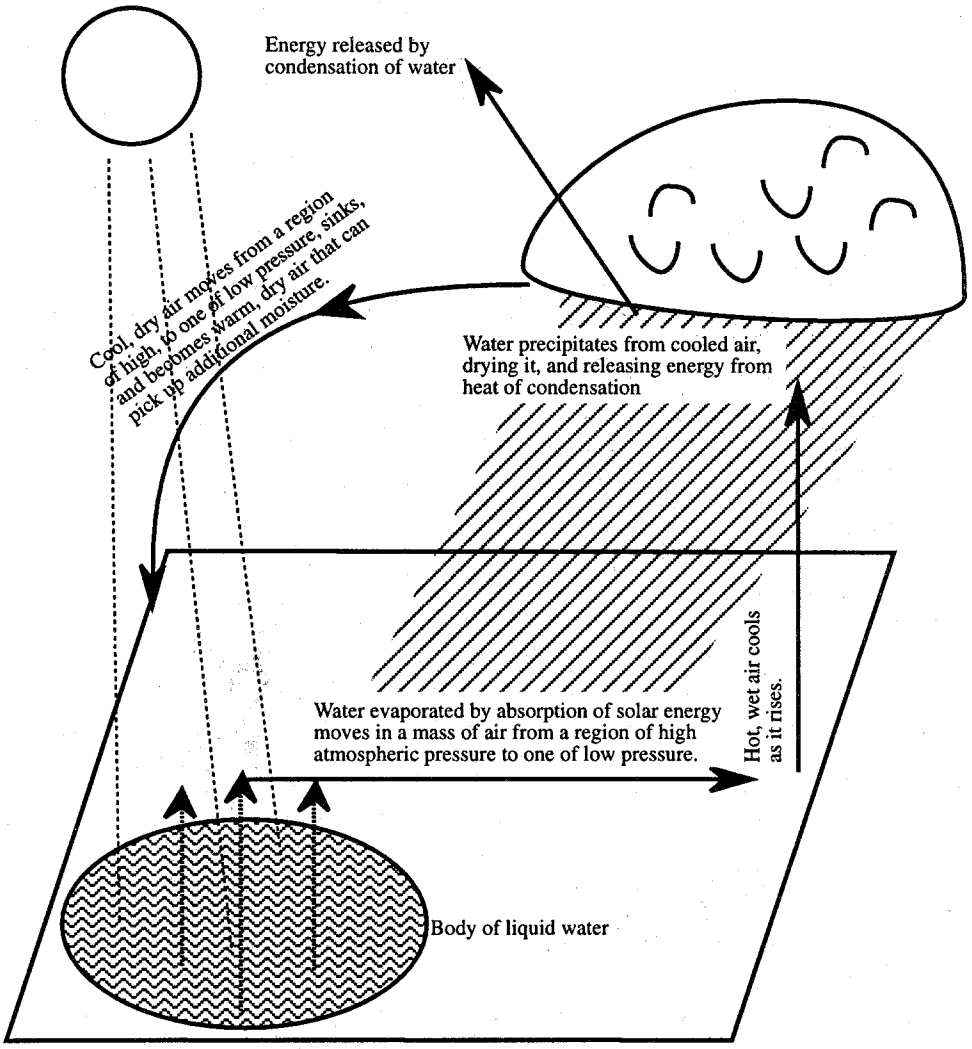


Figure 14.5 Circulation patterns involved with movement of air masses and water; uptake and release of solar energy as latent heat in water vapor.

absorbing atmosphere must be traversed, so that progressively less energy is received per unit area of Earth's surface. The net result is that equatorial regions receive a much greater share of solar radiation, progressively less is received farther from the Equator, and the poles receive a comparatively minuscule amount. The excess heat energy in the equatorial regions causes the air to rise. The air ceases to rise when it reaches the stratosphere because in the stratosphere the air becomes warmer with higher elevation. As the hot equatorial air rises in the troposphere, it cools by expansion and loss of water, then sinks again. The air circulation patterns in which this occurs are called **Hadley cells**. As shown in Figure 14.6, there are three

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major groupings of these cells, which result in very distinct climatic regions on Earth's surface. The air in the Hadley cells does not move straight north and south, but is deflected by earth's rotation and by contact with the rotating earth; this is the **Coriolis effect**, which results in spiral-shaped air circulation patterns called cyclonic or anticyclonic, depending upon the direction of rotation. These give rise to different directions of prevailing winds, depending on latitude. The boundaries between the massive bodies of circulating air shift markedly over time and season, resulting in significant weather instability.

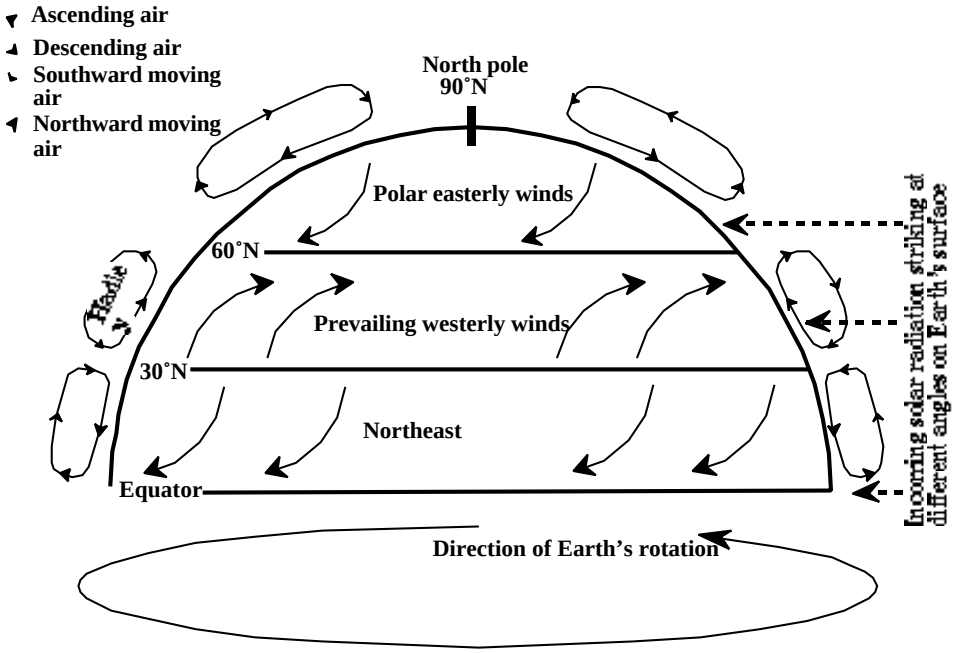


Figure 14.6 Global circulation of air in the northern hemisphere.

The movement of air in Hadley cells combines with other atmospheric phenomena to produce massive **jet streams** that are, in a sense, shifting rivers of air that may be several kilometers deep and several tens of km wide. Jet streams move through discontinuities in the tropopause (see Section 14.2), generally from west to east at velocities around 200 km/hr (well over 100 mph); in so doing, they redistribute huge amounts of air and have a strong influence on weather patterns.

The air and wind circulation patterns described above shift massive amounts of energy over long distances on Earth. If it weren't for this effect, the equatorial regions would be unbearably hot, and the regions closer to the poles intolerably cold. About half of the heat that is redistributed is carried as sensible heat by air circulation, almost 1/3 is carried by water vapor as latent heat, and the remaining approximately 20% is moved by ocean currents.

Weather Fronts and Storms

As noted earlier, the interface between two masses of air that differ in

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temperature, density, and water content is called a **front.** A mass of cold air moving such that it displaces one of warm air is a **cold front**, and a mass of warm air displacing one of cold air is a **warm front**. Since cold air is more dense than warm air, the air in a cold mass of air along a cold front pushes under warmer air. This causes the warm, moist air to rise such that water condenses from it. The condensation of water releases energy, so the air rises farther. The net effect can be formation of huge cloud formations (thunderheads) that may reach stratospheric levels. These spectacular thunderheads can produce heavy rainfall and even hail, and sometimes violent storms with strong winds, including tornadoes. Warm fronts cause somewhat similar effects as warm, moist air pushes over colder air. However, the front is usually much broader, and the weather effects milder, typically resulting in widespread drizzle rather than intense rainstorms.

Swirling **cyclonic storms**, such as typhoons, hurricanes, and tornadoes, are created in low pressure areas by rising masses of warm, moist air. As such air cools, water vapor condenses, and the latent heat released warms the air more, sustaining and intensifying its movement upward in the atmosphere. Air rising from surface level creates a low pressure zone into which surrounding air moves. The movement of the incoming air assumes a spiral pattern, thus causing a cyclonic storm.

14.6 INVERSIONS AND AIR POLLUTION

The complicated movement of air across the earth's surface is a crucial factor in the creation and dispersal of air pollution phenomena. When air movement ceases, stagnation can occur, with a resultant buildup of atmospheric pollutants in localized regions. Although the temperature of air relatively near the earth's surface normally decreases with increasing altitude, certain atmospheric conditions can result in the opposite condition—increasing temperature with increasing altitude. Such conditions are characterized by high atmospheric stability and are known as **temperature inversions**. Because they limit the vertical circulation of air, temperature inversions result in air stagnation and the trapping of air pollutants in localized areas.

Inversions can occur in several ways. In a sense, the whole atmosphere is inverted by the warm stratosphere, which floats atop the troposphere with relatively little mixing. An inversion can form from the collision of a warm air mass (warm front) with a cold air mass (cold front). The warm air mass overrides the cold air mass in the frontal area, producing the inversion. **Radiation inversions** are likely to form in still air at night when the earth is no longer receiving solar radiation. The air closest to the earth cools faster than the air higher in the atmosphere, which remains warm, thus less dense. Furthermore, cooler surface air tends to flow into valleys at night, where it is overlain by warmer, less dense air. **Subsidence inversions**, often accompanied by radiation inversions, can become very widespread. These inversions can form in the vicinity of a surface high pressure area when high-level air subsides to take the place of surface air blowing out of the high pressure zone. The subsiding air is warmed as it compresses and can remain as a warm layer several hundred meters above ground level. A **marine inversion** is produced during the summer months when cool air laden with moisture from the ocean blows onshore and under warm, dry inland air.

As noted above, inversions contribute significantly to the effects of air pollution

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because, as shown in Figure 14.7, they prevent mixing of air pollutants, thus keeping the pollutants in one area. This not only prevents the pollutants from escaping, but also acts like a container in which additional pollutants accumulate. Furthermore, in the case of secondary pollutants formed by atmospheric chemical processes, such as photochemical smog (see Chapter 16), the pollutants may be kept together such that they react with each other and with sunlight to produce even more noxious products.

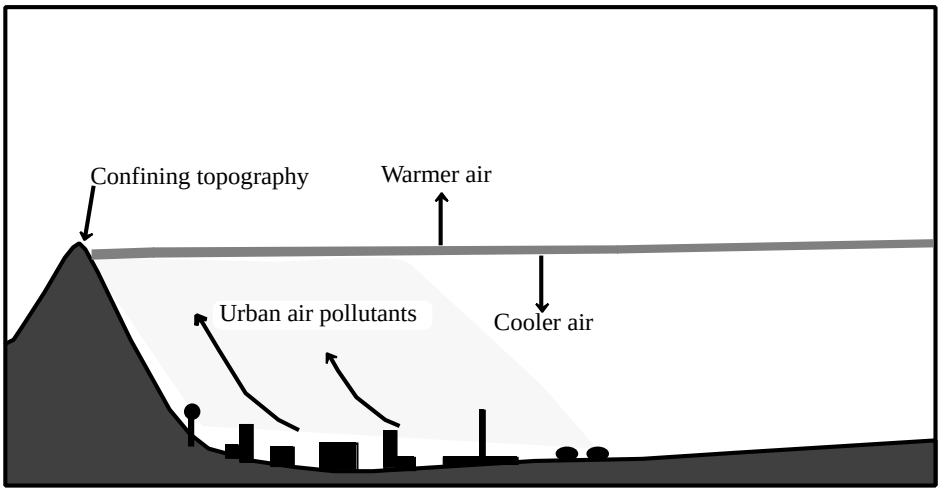


Figure 14.7 Illustration of pollutants trapped in a temperature inversion.

14.7 GLOBAL CLIMATE AND MICROCLIMATE

Perhaps the single most important influence on Earth's environment is **climate**, consisting of long-term weather patterns over large geographical areas. As a general rule, climatic conditions are characteristic of a particular region. This does not mean that climate remains the same throughout the year, of course, because it varies with season. One important example of such variation is the **monsoon**, seasonal variations in wind patterns between oceans and continents. The climates of Africa and the Indian subcontinent are particularly influenced by monsoons. In the latter, for example, summer heating of the Indian land mass causes air to rise, thereby creating a low pressure area that attracts warm, moist air from the ocean. This air rises on the slopes of the Himalayan mountains, which also block the flow of colder air from the north; moisture from the air condenses; and monsoon rains carrying enormous amounts of precipitation fall. Thus, from May until sometime into August, summer monsoon rains fall in India, Bangladesh, and Nepal. Reversal of the pattern of winds during the winter months causes these regions to have a dry season, but produces winter monsoon rains in the Philippine islands, Indonesia, New Guinea, and Australia.

Summer monsoon rains are responsible for tropical rain forests in Central Africa. The interface between this region and the Sahara Desert varies over time. When the boundary is relatively far north, rain falls on the Sahel desert region at the interface, crops grow, and the people do relatively well. When the boundary is more to the south, a condition that may last for several years, devastating droughts and even

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starvation may occur.

It is known that there are fluctuations, cycles, and cycles imposed on cycles in climate. The causes of these variations are not completely understood, but they are known to be substantial, and even devastating to civilization. The last **ice age**, which ended only about 10,000 years ago and which was preceded by several similar ice ages, produced conditions under which much of the present land mass of the Northern Hemisphere was buried under thick layers of ice and, thus, uninhabitable. A "mini-ice age" occurred during the 1300s, causing crop failures and severe hardship in northern Europe. In modern times, the El Niño Southern Oscillation occurs with a period of several years when a large, semi-permanent tropical low pressure area shifts into the Central Pacific region from its more common location in the vicinity of Indonesia. This shift modifies prevailing winds, changes the pattern of ocean currents, and affects upwelling of ocean nutrients with profound effects on weather, rainfall, and fish and bird life over a vast area of the Pacific from Australia to the west coasts of South and North America.

Human Modifications of Climate

Although Earth's atmosphere is huge and has an enormous ability to resist and correct for detrimental change, it is possible that human activities are reaching a point at which they may be adversely affecting climate. One such way is by emission of large quantities of carbon dioxide and other greenhouse gases into the atmosphere, such that global warming may occur and cause substantial climatic change. Another way is through the release of gases, particularly chlorofluorocarbons (Freons) that may cause destruction of vital stratospheric ozone. Human activities that may affect climate are addressed in the next two chapters.

Microclimate

The preceding section described climate on a large scale, ranging up to global dimensions. The climate that organisms and objects on the surface are exposed to close to the ground, under rocks, and surrounded by vegetation, is often quite different from the surrounding macroclimate. Such highly localized climatic conditions are termed the **microclimate**. Microclimate effects are largely determined by the uptake and loss of solar energy very close to Earth's surface, and by the fact that air circulation due to wind is much lower at the surface. During the day, solar energy absorbed by relatively bare soil heats the surface, but is lost only slowly because of very limited air circulation at the surface. This provides a warm blanket of surface air several cm thick, and an even thinner layer of warm soil. At night, radiative loss of heat from the surface of soil and vegetation can result in surface temperatures several degrees colder than the air about 2 meters above ground level. These lower temperatures result in condensation of **dew** on vegetation and the soil surface, thus providing a relatively more moist microclimate near ground level. Heat absorbed during early morning evaporation of the dew tends to prolong the period of cold experienced right at the surface.

Vegetation substantially affects microclimate. In relatively dense growths, circu-

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lation can be virtually zero at the surface because vegetation severely limits convection and diffusion. The crown surface of the vegetation intercepts most of the solar energy, so that maximum solar heating may be a significant distance up from Earth's surface. The region below the crown surface of vegetation thus becomes one of relatively stable temperature. In addition, in a dense growth of vegetation, most of the moisture loss is not from evaporation from the soil surface, but rather from transpiration from plant leaves. The net result is the creation of temperature and humidity conditions that provide a favorable living environment for a number of organisms, such as insects and rodents.

Another factor influencing microclimate is the degree to which the slope of land faces north or south. South-facing slopes of land in the Northern Hemisphere receive greater solar energy. Advantage has been taken of this phenomenon in restoring land strip-mined for brown coal in Germany by terracing the land such that the terraces have broad south slopes and very narrow north slopes. On the south-sloping portions of the terrace, the net effect has been to extend the short summer growing season by several days, thereby significantly increasing crop productivity. In areas where the growing season is longer, better growing conditions may exist on a north slope because it is less subject to temperature extremes and to loss of water by evaporation and transpiration.

Effects of Urbanization on Microclimate

A particularly marked effect on microclimate is that induced by urbanization. In a rural setting, vegetation and bodies of water have a moderating effect, absorbing modest amounts of solar energy and releasing it slowly. The stone, concrete, and asphalt pavement of cities have an opposite effect, strongly absorbing solar energy, and re-radiating heat back to the urban microclimate. Rainfall is not allowed to accumulate in ponds, but is drained away as rapidly and efficiently as possible. Human activities generate significant amounts of heat, and produce large quantities of CO_2 and other greenhouse gases that retain heat. The net result of these effects is that a city is capped by a **heat dome** in which the temperature is as much as 5˚C warmer than in the surrounding rural areas, such that large cities have been described as "heat islands." The rising warmer air over a city brings in a breeze from the surrounding area and causes a local greenhouse effect that probably is largely counterbalanced by reflection of incoming solar energy by particulate matter above cities. Overall, compared with climatic conditions in nearby rural surroundings, the city microclimate is warmer, foggier, overlain with more cloud cover a greater percentage of the time, and subject to more precipitation, though generally the city microclimate is less humid.

14.8 CHEMICAL AND PHOTOCHEMICAL REACTIONS IN THE ATMOSPHERE

Figure 14.8 represents some of the major atmospheric chemical processes, which are discussed under the topic of atmospheric chemistry. The study of atmospheric chemical reactions is difficult. One of the primary obstacles encountered in studying atmospheric chemistry is that the chemist generally must deal with

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incredibly low concentrations, so that the detection and analysis of reaction products is quite difficult. Simulating high-altitude conditions in the laboratory can be extremely hard because of interferences, such as those from species given off from container walls under conditions of very low pressure. Many chemical reactions that require a third body to absorb excess energy occur very slowly in the upper atmosphere where there is a sparse concentration of third bodies, but occur readily in a container whose walls effectively absorb energy. Container walls may serve as catalysts for some important reactions, or they may absorb important species and react chemically with the more reactive ones.

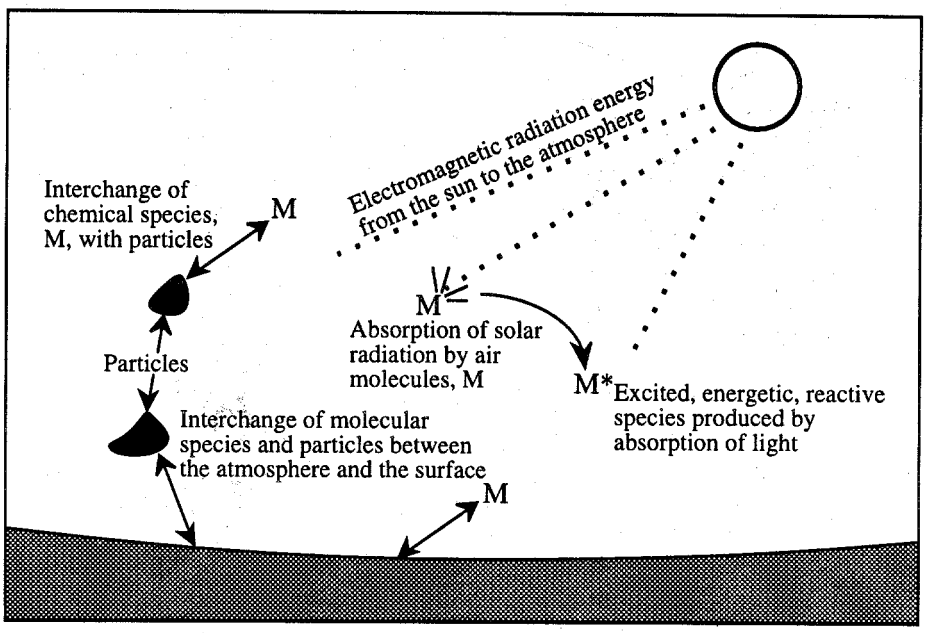


Figure 14.8 Representation of major atmospheric chemical processes.

Atmospheric chemistry involves the unpolluted atmosphere, highly polluted atmospheres, and a wide range of gradations in between. The same general phenomena govern all and produce one huge atmospheric cycle in which there are numerous subcycles. Gaseous atmospheric chemical species fall into the following somewhat arbitrary and overlapping classifications: Inorganic oxides (CO, CO_2, NO_2, SO_2), oxidants (O_3, H_2O_2, HO• radical, HO_2• radical, ROO• radicals, NO_3), reductants (CO, SO_2, H_2S), organics (also reductants; in the unpolluted atmosphere, CH_4 is the predominant organic species, whereas alkanes, alkenes, and aryl compounds are common around sources of organic pollution), oxidized organic species (carbonyls, organic nitrates), photochemically active species (NO_2, formaldehyde), acids (H_2SO_4), bases (NH_3), salts (NH_4HSO_4,), and unstable reactive species (electronically excited NO_2, HO• radical). Both solid and liquid particles in atmospheric aerosols and clouds serve as sources and sinks for gas-phase species, as sites for surface reactions (solid particles), and as bodies for aqueous-phase reactions (liquid droplets). Two constituents of utmost importance in atmospheric chemistry are radiant energy from the sun, predominantly in the ultraviolet region of the spectrum,

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and the hydroxyl radical, HO•. The former provides a way to pump a high level of energy into a single gas molecule to start a series of atmospheric chemical reactions, and the latter is the most important reactive intermediate and "currency" of daytime atmospheric chemical phenomena; NO_3 radicals are important intermediates in nightime atmospheric chemistry.

Photochemical Processes

The absorption by chemical species of light, broadly defined here to include ultraviolet radiation from the sun, can bring about reactions, called **photochemical reactions**, which do not otherwise occur under the conditions (particularly the temperature) of the medium in the absence of light. Thus, photochemical reactions, even in the absence of a chemical catalyst, occur at temperatures much lower than those that otherwise would be required. Photochemical reactions, which are induced by intense solar radiation, play a very important role in determining the nature and ultimate fate of a chemical species in the atmosphere.

Nitrogen dioxide, NO_2, is one of the most photochemically active species found in a polluted atmosphere and is an essential participant in the smog-formation process. A species such as NO_2 may absorb light of energy $h\nu$, producing an **electronically excited molecule**,

$$NO_2 + h\nu \rightarrow NO_2^* \qquad (14.8.1)$$

designated in the reaction above by an asterisk, *. The photochemistry of nitrogen dioxide is discussed in greater detail in Chapters 15 and 16.

Electronically excited molecules are one of the three relatively reactive and unstable species that are encountered in the atmosphere and are strongly involved with atmospheric chemical processes. The other two species are atoms or molecular fragments with unshared electrons, called **free radicals**, and **ions** consisting of electrically charged atoms or molecular fragments.

Electronically excited molecules are produced when stable molecules absorb energetic electromagnetic radiation in the ultraviolet or visible regions of the spectrum. A molecule can possess several possible excited states, but generally ultraviolet or visible radiation is energetic enough to excite molecules only to several of the lowest energy levels. The nature of the excited state can be understood by considering the disposition of electrons in a molecule. Most molecules have an even number of electrons. The electrons occupy orbitals (see orbitals of atoms in Chapter 3, Section 3.12), with a maximum of two electrons with opposite spin occupying the same orbital. The absorption of light may promote one of these electrons to a vacant orbital of higher energy. In some cases the electron thus promoted retains a spin opposite to that of its former partner, giving rise to an **excited singlet state**. In other cases the spin of the promoted electron is reversed, such that it has the same spin as its former partner; this gives rise to an **excited triplet state**. These phenomena are illustrated in Figure 14.9.

These excited states generated by the absorption of electromagnetic radiation are relatively energized compared with the ground state and are chemically reactive species. Their participation in atmospheric chemical reactions, such as those

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involved in smog formation, will be discussed later in detail.

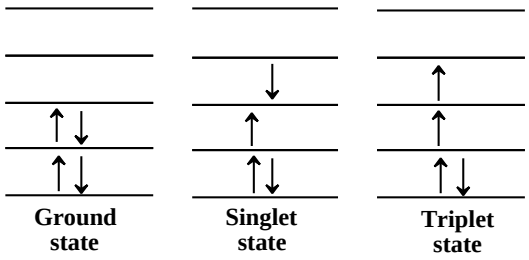


Figure 14.9 Representation of major atmospheric chemical processes.

For a photochemical reaction to occur, light must be absorbed by the reacting species. If the absorbed light is in the visible region of the sun's spectrum, the absorbing species is colored. Colored NO_2 is a common example of such a species in the atmosphere. Normally, the first step in a photochemical process is the activation of the molecule by the absorption of a single unit of photochemical energy characteristic of the frequency of the electromagnetic radiation (commonly ultraviolet radiation or visible light) called a **quantum** of electromagnetic radiation. The energy of one quantum is equal to the product $h\nu$, where h is Planck's constant, 6.63×10^{-27} erg·s (6.63×10 J·s), and ν is the frequency of the absorbed electromagnetic radiation in s^{-1} (inversely proportional to its wavelength, λ).

The reactions that occur following absorption of a photon of electromagnetic radiation to produce an electronically excited species are largely determined by the way in which the excited species loses its excess energy. This can occur by one of the following processes:

- Loss of energy to another molecule or atom (M) by **physical quenching**, followed by dissipation of the energy as heat

$$O_2^* + M \rightarrow O_2 + M(\text{higher translational energy}) \qquad (14.8.2)$$

- **Dissociation** of the excited molecule (the process responsible for the predominance of atomic oxygen in the upper atmosphere)

$$O_2^* \rightarrow O + O \qquad (14.8.3)$$

- **Direct reaction** with another species

$$O_2^* + O_3 \rightarrow 2O_2 + O \qquad (14.8.4)$$

- **Luminescence** consisting of loss of energy by the emission of electromagnetic radiation

$$NO_2^* \rightarrow NO_2 + h\nu \qquad (14.8.5)$$

If the re-emission of light is almost instantaneous, luminescence is called

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fluorescence, and if it is significantly delayed, the phenomenon is **phosphorescence**. **Chemiluminescence** is said to occur when the excited species (such as NO_2* below) is formed by a chemical process:

$$O_3 + NO \rightarrow NO_2^* + O_2(\text{higher energy}) \qquad (14.8.6)$$

- **Intermolecular energy transfer** in which an excited species transfers energy to another species that then becomes excited

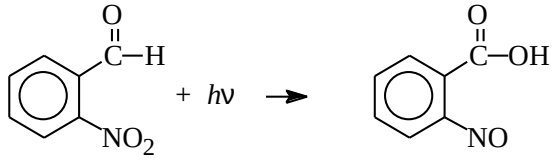
$$O_2^* + Na \rightarrow O_2 + Na^* \qquad (14.8.7)$$

A subsequent reaction by the second species is called a **photosensitized** reaction.

- **Intramolecular transfer** in which energy is transferred within a molecule

$$XY^* \rightarrow XY^{\dagger}(\text{where } {}^{\dagger} \text{ denotes another excited state of the same molecule}) \qquad (14.8.8)$$

- **Spontaneous isomerization** as in the conversion of *o*-nitrobenzaldehyde to *o*-nitrosobenzoic acid, a reaction used in chemical actinometers to measure exposure to electromagnetic radiation:



(14.8.9)

- **Photoionization** through loss of an electron

$$N_2^* \rightarrow N_2^+ + e^- \qquad (14.8.10)$$

Electromagnetic radiation absorbed in the infrared region lacks the energy to break chemical bonds, but does cause the receptor molecules to gain vibrational and rotational energy. The energy absorbed as infrared radiation ultimately is dissipated as heat and raises the temperature of the whole atmosphere. As noted in Section 14.3, the absorption of infrared radiation is very important in the earth's acquiring heat from the sun and in the retention of energy radiated from the earth's surface.

Ions and Radicals in the Atmosphere

One of the characteristics of the upper atmosphere that is difficult to duplicate under laboratory conditions is the presence of significant levels of electrons and positive ions. Because of the rarefied conditions, these ions may exist in the upper atmosphere for long periods before recombining to form neutral species.

At altitudes of approximately 50 km and up, ions are so prevalent that the region is called the **ionosphere**. The presence of the ionosphere has been known since about 1901, when it was discovered that radio waves could be transmitted over long dis-

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tances where the curvature of the earth makes line-of-sight transmission impossible. These radio waves bounce off the ionosphere.

Ultraviolet light is the primary producer of ions in the ionosphere. In darkness, the positive ions slowly recombine with free electrons. The process is more rapid in the lower regions of the ionosphere, where the concentration of species is relatively high. Thus, the lower limit of the ionosphere lifts at night and makes possible the transmission of radio waves over much greater distances.

The earth's magnetic field has a strong influence upon the ions in the upper atmosphere. Probably the best-known manifestation of this phenomenon is found in the Van Allen belts, discovered in 1958, consisting of two belts of ionized particles encircling the earth. They can be visualized as two doughnuts with the axis of Earth's magnetic field extending through the holes in the doughnuts. The inner belt consists of protons and the outer belt consists of electrons. A schematic diagram of the Van Allen belts is shown in Figure 14.10.

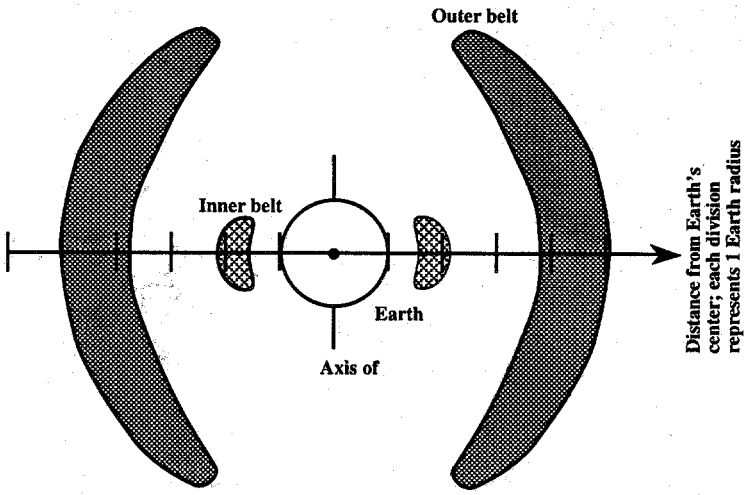


Figure 14.10 Cross section of the Van Allen belts encircling the Earth.

Although ions are produced in the upper atmosphere primarily by the action of energetic electromagnetic radiation, they can also be produced in the troposphere by the shearing of water droplets during precipitation. The shearing may be caused by the compression of descending masses of cold air or by strong winds over hot, dry land masses. The last phenomenon is known as the *foehn*, *sharav* (in the Near East), or Santa Ana (in southern California). These hot, dry winds cause severe discomfort. The ions they produce consist of electrons and positively charged molecular species.

Free Radicals

In addition to forming ions by photoionization, energetic electromagnetic radiation in the atmosphere may produce atoms or groups of atoms with unpaired electrons called **free radicals**:

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(14.8.11)

Free radicals are involved with most significant atmospheric chemical phenomena and are of the utmost importance in the atmosphere. Because of their unpaired electrons and the strong pairing tendencies of electrons under most circumstances, free radicals are highly reactive. The upper atmosphere is so rarefied, however, that at very high altitudes, radicals may have half-lives of several minutes, or even longer. Radicals can take part in chain reactions in which one of the products of each reaction is a radical. Eventually, through processes such as reaction with another radical, one of the radicals in a chain is destroyed and the chain ends, as shown by the reaction of two methyl ($H_3C\bullet$) radicals below:

$$H_3C\bullet + H_3C\bullet \rightarrow C_2H_6 \qquad (14.8.12)$$

This process is a **chain-terminating reaction**. Reactions involving free radicals are responsible for photochemical smog formation. These processes are discussed in Chapter 16.

Free radicals are quite reactive; therefore, they generally have short lifetimes. It is important to distinguish between high reactivity and instability. A totally isolated free radical or atom would be quite stable. Therefore, free radicals and single atoms from diatomic gases tend to persist under the rarefied conditions of very high altitudes because they can travel long distances before colliding with another reactive species. However, electronically excited species have a finite, generally very short lifetime because they can lose energy through radiation without having to react with another species.

Hydroxyl and Hydroperoxyl Radicals in the Atmosphere

The hydroxyl radical, $HO\bullet$, is the single most important reactive intermediate species in atmospheric chemical processes. It is formed by several mechanisms. At higher altitudes, it is produced by photolysis of water:

$$H_2O + h\nu \rightarrow HO\bullet + H \qquad (14.8.13)$$

In the presence of organic matter, hydroxyl radical is produced in abundant quantities as an intermediate in the formation of photochemical smog (see Chapter 16). To a certain extent in the atmosphere, and for laboratory experimentation, $HO\bullet$ is made by the photolysis of nitrous acid vapor:

$$HONO + h\nu \rightarrow HO\bullet + NO \qquad (14.8.14)$$

In the relatively unpolluted troposphere, hydroxyl radical is produced as the result of the photolysis of ozone,

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$$O_3 + h\nu(\lambda < 315\ \text{nm}) \rightarrow O^* + O_2 \quad (14.8.15)$$

followed by the reaction of a fraction of the excited oxygen atoms with water molecules:

$$O^* + H_2O \rightarrow 2HO\bullet \quad (14.8.16)$$

Hydroxyl radical is a key species in chemical transformations of a number of trace species in the atmosphere. Some aspects of the involvement of hydroxyl radical in such transformations are discussed in the next two chapters. Among the important atmospheric trace species that react with hydroxyl radical are carbon monoxide, sulfur dioxide, hydrogen sulfide, methane, and nitric oxide.

Hydroxyl radical is most frequently removed from the troposphere by reaction with methane or carbon monoxide:

$$CH_4 + HO\bullet \rightarrow H_3C\bullet + H_2O \quad (14.8.17)$$

$$CO + HO\bullet \rightarrow CO_2 + H \quad (14.8.18)$$

The highly reactive methyl radical, $H_3C\bullet$, reacts with O_2,

$$H_3C\bullet + O_2 \rightarrow H_3COO\bullet \quad (14.8.19)$$

to form **methylperoxyl radical**, $H_3COO\bullet$. (Further reactions of this species are discussed in Chapter 16.) The hydrogen atom produced in Reaction 14.8.17 reacts with O_2 to produce **hydroperoxyl radical**:

$$H + O_2 \rightarrow HOO\bullet \quad (14.8.20)$$

The hydroperoxyl radical can undergo chain termination reactions, such as

$$HOO\bullet + HO\bullet \rightarrow H_2O + O_2 \quad (14.8.21)$$

$$HOO\bullet + HOO\bullet \rightarrow H_2O_2 + O_2 \quad (14.8.22)$$

or reactions that regenerate hydroxyl radical:

$$HOO\bullet + NO \rightarrow NO_2 + HO\bullet \quad (14.8.23)$$

$$HOO\bullet + O_3 \rightarrow 2O_2 + HO\bullet \quad (14.8.24)$$

The global concentration of hydroxyl radical, averaged diurnally and seasonally, is estimated to range from 2×10^5 to 1×10^6 radicals per cm^3 in the troposphere. Because of the higher humidity and higher incident sunlight, which result in elevated O* levels, the concentration of $HO\bullet$ is higher in tropical regions. The Southern Hemisphere probably has about a 20% higher level of $HO\bullet$ than does the Northern Hemisphere because of greater production of anthropogenic, $HO\bullet$-consuming CO in

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the Northern Hemisphere.

The hydroperoxyl radical, HOO•, is an intermediate in some important chemical reactions. In addition to its production by the reactions discussed above, in polluted atmospheres, hydroperoxyl radical is made by the following two reactions, starting with photolytic dissociation of formaldehyde to produce a reactive formyl radical:

$$HCHO + h\nu \rightarrow H + \dot{H}CO \quad (14.8.25)$$

$$\dot{H}CO + O_2 \rightarrow HOO^{\bullet} + CO \quad (14.8.26)$$

The hydroperoxyl radical reacts more slowly with other species than does the hydroxyl radical. The kinetics and mechanisms of hydroperoxyl radical reactions are difficult to study because it is hard to retain these radicals free of hydroxyl radicals.

Chemical and Biochemical Processes in Evolution of the Atmosphere

It is now widely believed that the earth's atmosphere originally was very different from its present state and that the changes were brought about by biological activity and accompanying chemical changes. Approximately 3.5 billion years ago, when the first primitive life molecules were formed, the atmosphere was probably free of oxygen and consisted of a variety of gases such as carbon dioxide, water vapor, and perhaps even methane, ammonia, and hydrogen. The atmosphere was bombarded by intense, bond-breaking ultraviolet light which, along with lightning and radiation from radionuclides, provided the energy to bring about chemical reactions that resulted in the production of relatively complicated molecules, including even amino acids and sugars, which are produced and used by living organisms. From the rich chemical mixture in the sea, life molecules evolved. Initially, these very primitive life forms derived their energy from fermentation of organic matter formed by chemical and photochemical processes, but eventually they gained the capability to produce organic matter, "$\{CH_2O\}$," by photosynthesis:

$$CO_2 + H_2O + h\nu \rightarrow \{CH_2O\} + O_2(g) \quad (14.8.27)$$

Photosynthesis released oxygen, thereby setting the stage for the massive biochemical transformation that resulted in the production of almost all the atmosphere's O_2.

The elemental oxygen initially produced by photosynthesis was probably quite toxic to primitive life forms. However, much of this oxygen was converted to iron oxides by reaction with soluble iron(II):

$$4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+ \quad (14.8.28)$$

The existence of enormous deposits of iron oxides provides major evidence for the liberation of free O_2 in the primitive atmosphere.

Eventually, enzyme systems developed that enabled organisms to mediate the reaction of waste-product oxygen with oxidizable organic matter in the sea. Later, this mode of waste-product disposal was utilized by organisms to produce energy by respiration, which is now the mechanism by which nonphotosynthetic organisms

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obtain energy.

In time, O_2 accumulated in the atmosphere, providing an abundant source of oxygen for respiration. It had an additional benefit in that it enabled the formation of an ozone shield (see Section 14.10). The ozone shield absorbs bond-rupturing ultraviolet light. With the ozone shield protecting tissue from destruction by high-energy ultraviolet radiation, the earth became a much more hospitable environment for life, and life forms were enabled to move from the sea to land.

14.9 ACID-BASE REACTIONS IN THE ATMOSPHERE

Acid-base reactions occur between acidic and basic species in the atmosphere. The atmosphere is normally at least slightly acidic because of the presence of a low level of carbon dioxide, which dissolves in atmospheric water droplets and dissociates slightly:

$$CO_2(g) \xrightarrow{\text{water}} CO_2(aq) \qquad (14.9.1)$$

$$CO_2(aq) + H_2O \rightarrow H^+ + HCO_3^- \qquad (14.9.2)$$

Atmospheric sulfur dioxide forms a somewhat stronger acid when it dissolves in water:

$$SO_2(g) + H_2O \rightarrow H^+ + HSO_3^- \qquad (14.9.3)$$

In terms of pollution, however, strongly acidic HNO_3 and H_2SO_4 formed by the atmospheric oxidation of N oxides, SO_2, and H_2S are much more important because they lead to the formation of damaging acid rain (see Chapter 15).

As reflected by the generally acidic pH of rainwater, basic species are relatively less common in the atmosphere. Particulate calcium oxide, hydroxide, and carbonate can get into the atmosphere from ash and ground rock, and can react with acids such as in the following reaction:

$$Ca(OH)_2(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + 2H_2O \qquad (14.9.4)$$

The most important basic species in the atmosphere is gas-phase ammonia, NH_3. The major source of atmospheric ammonia is from biodegradation of nitrogen-containing biological matter and from bacterial reduction of nitrate:

$$NO_3^-(aq) + 2\{CH_2O\}(biomass) + H^+ \rightarrow NH_3(g) + 2CO_2 + H_2O \qquad (14.9.5)$$

Ammonia is particularly important as a base in the air because it is the only water-soluble base present at significant levels in the atmosphere. When it is dissolved in atmospheric water droplets, ammonia plays a strong role in neutralizing atmospheric acids, as shown by the following reactions:

$$NH_3(aq) + HNO_3(aq) \rightarrow NH_4NO_3(aq) \qquad (14.9.6)$$

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$$NH_3(aq) + H_2SO_4(aq) \rightarrow NH_4HSO_4(aq) \qquad (14.9.7)$$

These reactions have three effects: (1) They result in the presence of NH_4^+ ion in the atmosphere as dissolved or solid salts, (2) they serve in part to neutralize acidic consituents of the atmosphere, and (3) they produce relatively corrosive ammonium salts.

14.10 REACTIONS OF ATMOSPHERIC OXYGEN

Some of the primary features of the exchange of oxygen among the atmosphere, geosphere, hydrosphere, and biosphere are summarized in Figure 14.11. The oxygen cycle is critically important in atmospheric chemistry, geochemical transformations, and life processes.

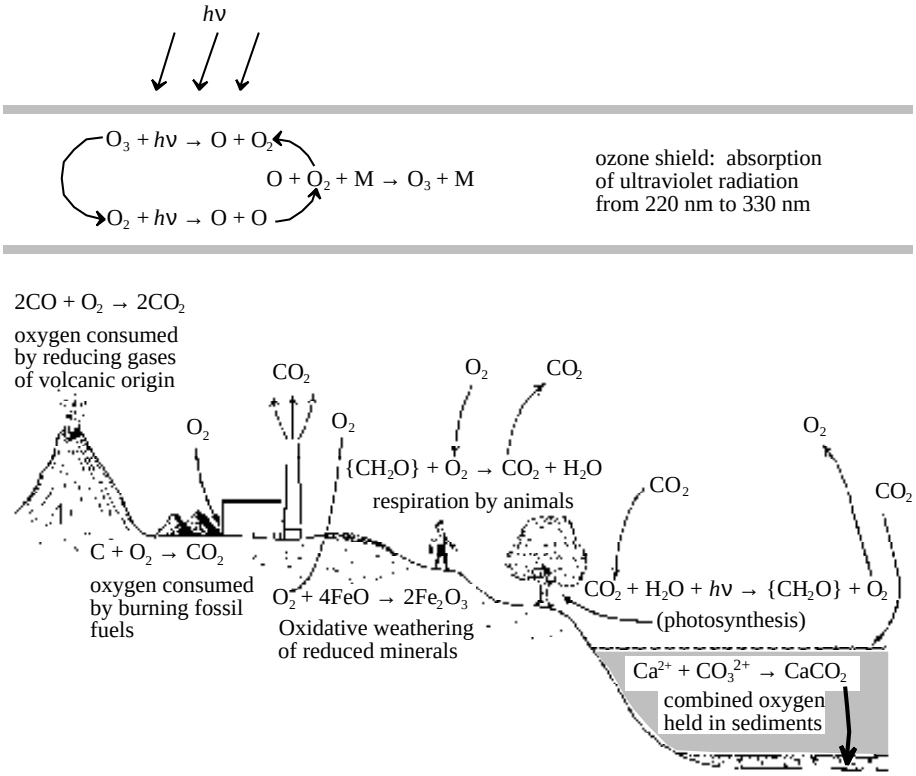


Figure 14.11 Oxygen exchange among the atmosphere, geosphere, hydrosphere, and biosphere.

Oxygen in the troposphere plays a strong role in processes that occur on the earth's surface. Atmospheric oxygen takes part in energy-producing reactions, such as the burning of fossil fuels:

$$CH_4(\text{in natural gas}) + 2O_2 \rightarrow CO_2 + 2H_2O \qquad (14.10.1)$$

Atmospheric oxygen is utilized by aerobic organisms in the degradation of organic

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material. Some oxidative weathering processes consume oxygen, such as

$$4FeO + O_2 \rightarrow 2Fe_2O_3 \quad (14.10.2)$$

Oxygen is returned to the atmosphere through plant photosynthesis:

$$CO_2 + H_2O + h\nu \rightarrow \{CH_2O\} + O_2 \quad (14.10.3)$$

All molecular oxygen now in the atmosphere is thought to have originated through the action of photosynthetic organisms, which shows the importance of photosynthesis in the oxygen balance of the atmosphere. It can be shown that most of the carbon fixed by these photosynthetic processes is dispersed in mineral formations as humic material (see Chapter 11, Section 11.9); only a very small fraction is deposited in fossil fuel beds. Therefore, although combustion of fossil fuels consumes large amounts of O_2, there is no danger of running out of atmospheric oxygen.

Molecular oxygen is somewhat unusual in that its ground state is a triplet state with two unpaired electrons, designated here as $^3O_2$, which can be excited to singlet molecular oxygen, designated here as $^1O_2$. The latter can be produced by several processes, including direct photochemical excitation, transfer of energy from other electronically excited molecules, ozone photolysis, and high-energy oxygen-producing reactions.

Because of the extremely rarefied atmosphere and the effects of ionizing radiation, elemental oxygen in the upper atmosphere exists to a large extent in forms other than diatomic O_2. In addition to O_2, the upper atmosphere contains oxygen atoms, O; excited oxygen molecules, O_2*; and ozone, O_3.

Atomic oxygen, O, is stable primarily in the thermosphere, where the atmosphere is so rarefied that the three-body collisions necessary for the chemical reaction of atomic oxygen seldom occur (the third body in this kind of three-body reaction absorbs energy to stabilize the products). Atomic oxygen is produced by a photochemical reaction:

$$O_2 + h\nu \rightarrow O + O \quad (14.10.4)$$

The oxygen-oxygen bond is strong (120 kcal/mole) and ultraviolet radiation in the wavelength regions 135–176 nm and 240–260 nm is most effective in causing dissociation of molecular oxygen. Because of photochemical dissociation, O_2 is virtually nonexistent at very high altitudes and less than 10% of the oxygen in the atmosphere at altitudes exceeding approximately 400 km is present in the molecular form. At altitudes exceeding about 80 km, the average molecular weight of air is lower than the 28.97 g/mole observed at sea level because of the high concentration of atomic oxygen. The resulting division of the atmosphere into a lower section with a uniform molecular weight and a higher region with a nonuniform molecular weight is the basis for classifying these two atmospheric regions as the **homosphere** and **heterosphere**, respectively.

Oxygen atoms in the atmosphere can exist in the ground state (O) and in excited states (O*). These are produced by the photolysis of ozone, which has a relatively

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weak bond energy of 26 kcal/mole at wavelengths below 308 nm,

$$O_3 + h\nu(\lambda < 308 \text{ nm}) \rightarrow O^* + O_2 \quad (14.10.5)$$

or by highly energetic chemical reactions such as

$$O + O + O \rightarrow O_2 + O^* \quad (14.10.6)$$

Excited atomic oxygen emits visible light at wavelengths of 636 nm, 630 nm, and 558 nm. This emitted light is partially responsible for **airglow**, a very faint electromagnetic radiation continuously emitted by the earth's atmosphere. Although its visible component is extremely weak, airglow is quite intense in the infrared region of the spectrum.

Oxygen ion, O^+, which may be produced by ultraviolet radiation acting upon oxygen atoms,

$$O + h\nu \rightarrow O^+ + e^- \quad (14.10.7)$$

is the predominant positive ion in some regions of the ionosphere. Other oxygen-containing ions in the ionosphere are O_2^+ and NO^+.

Ozone, O_3, has an essential protective function because it absorbs harmful ultraviolet radiation in the stratosphere and serves as a radiation shield, protecting living beings on the earth from the effects of excessive amounts of such radiation. It is produced by a photochemical reaction,

$$O_2 + h\nu \rightarrow O + O \quad (14.10.8)$$

(where the wavelength of the exciting radiation must be less than 242.4 nm), followed by a three-body reaction,

$$O + O_2 + M \rightarrow O_3 + M(\text{increased energy}) \quad (14.10.9)$$

in which M is another species, such as a molecule of N_2 or O_2, which absorbs the excess energy given off by the reaction and enables the ozone molecule to stay together. The region of maximum ozone concentration is found within the range of 25–30 km high in the stratosphere where it may reach 10 ppm.

Ozone absorbs ultraviolet light very strongly in the region 220–330 nm. If this light were not absorbed by ozone, severe damage would result to exposed forms of life on the earth. Absorption of electromagnetic radiation by ozone converts the radiation's energy to heat and is responsible for the temperature maximum encountered at the boundary between the stratosphere and the mesosphere at an altitude of approximately 50 km. The reason that the temperature maximum occurs at a higher altitude than that of the maximum ozone concentration arises from the fact that ozone is such an effective absorber of ultraviolet light. Therefore, most of the ultraviolet radiation absorbed by ozone is absorbed in the upper stratosphere, where it generates heat, and only a small fraction reaches the lower altitudes, which remain relatively cool.

The overall reaction,

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$$2O_3 \rightarrow 3O_2 \quad (14.10.10)$$

is favored thermodynamically so that ozone is inherently unstable. Its decomposition in the stratosphere is catalyzed by a number of natural and pollutant trace constituents, including NO, NO_2, H, $HO^{\bullet}$, $HOO^{\bullet}$, ClO, Cl, Br, and BrO. Ozone decomposition also occurs on solid surfaces, such as metal oxides and salts produced by rocket exhausts.

Despite its essential protective role in the stratosphere, ozone is an undesirable pollutant in the troposphere. It is toxic to animals and plants (see Chapter 23), and it also damages materials, particularly rubber.

14.11 REACTIONS OF ATMOSPHERIC NITROGEN

The 78% by volume of nitrogen contained in the atmosphere constitutes an inexhaustible reservoir of that essential element. The nitrogen cycle and nitrogen fixation by microorganisms were discussed in Chapter 6. A significant amount of nitrogen is fixed in the atmosphere by lightning, which provides the high energy needed to dissociate stable molecules of N_2. Some nitrogen is also fixed by combustion processes, particularly in internal combustion and turbine engines.

Before the use of synthetic fertilizers reached its current high levels, chemists were concerned that denitrification processes in the soil would lead to nitrogen depletion on the Earth. Now, with millions of tons of synthetically fixed nitrogen being added to the soil each year, major concern has shifted to possible excess accumulation of nitrogen in soil, fresh water, and the oceans.

Unlike oxygen, which is almost completely dissociated to the monatomic form in higher regions of the thermosphere, molecular nitrogen is not readily dissociated by ultraviolet radiation. However, at altitudes exceeding approximately 100 km, atomic nitrogen is produced by photochemical reactions:

$$N_2 + h\nu \rightarrow N + N \quad (14.11.1)$$

Nitric oxide, NO, is involved in the removal of stratospheric ozone and is regenerated by the reaction of NO_2 with atomic O, itself a precursor to the formation of ozone. An ion formed from NO, the NO^+ ion, is one of the predominant ionic species in the so-called E region of the ionosphere.

Pollutant oxides of nitrogen, particularly NO_2, are key species involved in air pollution and the formation of photochemical smog. For example, NO_2 is readily dissociated photochemically to NO and reactive atomic oxygen:

$$NO_2 + h\nu \rightarrow NO + O \quad (14.11.2)$$

This reaction is the most important primary photochemical process involved in smog formation. The roles played by nitrogen oxides in smog formation and other forms of air pollution are discussed in Chapter 16.

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14.12 ATMOSPHERIC WATER

The water vapor content of the troposphere is normally within a range of 1–3% by volume with a global average of about 1%. However, air can contain as little as 0.1% or as much as 5% water. The percentage of water in the atmosphere decreases rapidly with increasing altitude. Water circulates through the atmosphere in the hydrologic cycle as shown in Figure 3.1.

Water vapor absorbs infrared radiation even more strongly than does carbon dioxide, thus greatly influencing the earth's heat balance. Clouds formed from water vapor reflect light from the sun and have a temperature-lowering effect. On the other hand, water vapor in the atmosphere acts as a kind of "blanket" at night, retaining heat from the earth's surface by absorption of infrared radiation.

As discussed in Section 14.5, water vapor and the heat released and absorbed by transitions of water between the vapor state and liquid or solid are strongly involved in atmospheric energy transfer. Condensed water vapor in the form of very small droplets is of considerable concern in atmospheric chemistry. The harmful effects of some air pollutants—for instance, the corrosion of metals by acid-forming gases—requires the presence of water, which may come from the atmosphere. Atmospheric water vapor has an important influence upon pollution-induced fog formation under some circumstances. Water vapor interacting with pollutant particulate matter in the atmosphere may reduce visibility to undesirable levels through the formation of very small atmospheric aerosol particles.

As noted in Section 14.2, the cold tropopause serves as a barrier to the movement of water into the stratosphere. Thus, little water is transferred from the troposphere to the stratosphere, and the main source of water in the stratosphere is the photochemical oxidation of methane:

$$CH_4 + 2O_2 + h\nu \xrightarrow[\text{(several steps)}]{} CO_2 + 2H_2O \qquad (14.12.1)$$

The water thus produced serves as a source of stratospheric hydroxyl radical as shown by the following reaction:

$$H_2O + h\nu \rightarrow HO\bullet + H \qquad (14.12.2)$$

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Including water, the five most common gases in the atmosphere listed in decreasing order of their abundance are [1]_____. The bottom layer of the atmosphere is the [2]_____ and the next layer up is called the [3]_____. The most significant feature of atmospheric chemistry is the occurrence of [4]_____ resulting from the absorption by molecules of [5]_____. designated [6]_____.

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In addition to its essential role in protecting organisms from [7]_____, the atmosphere serves as a source of carbon dioxide for [8]_____ and molecular oxygen used by organisms for [9]_____. The important atmospheric trace gases are [10]_____. At very high altitudes, normally reactive species such as atomic oxygen, O, persist for long periods of time because [11]_____ _____. The fact that hydrogen has not been lost to outer space from Earth's atmosphere is due to the existence of [12]_____. The value of the solar constant is [13]_____. The three means for moving heat energy through the atmosphere are [14]_____ _____. The maximum intensity of incoming solar radiation occurs at a wavelength around [15]_____ and outgoing radiation from Earth has maximum intensity at a wavelength of around [16]_____. Water and carbon dioxide keep Earth warm by [17]_____. Albedo refers to [18]_____ _____. Meteorology is the study of [19]_____. Short-term variations in the state of the atmosphere constitute [20]_____ defined in terms of [21]_____ _____. Longer-term variations and trends within a particular geographical region in the factors just mentioned are described as [22]_____. Water vapor is particularly important in transferring energy in the atmosphere because it carries energy in the form of [23]_____. An atmospheric condition that is particularly important for air pollution and sometimes affected by topography is that of [24]_____. A heat dome over cities is an example of [25]_____. Photochemical reactions may be initiated when molecules split apart by absorbing [26]_____ to produce [27]_____. Major categories of gaseous atmospheric chemical species are [28]_____ _____ _____. An atmospheric molecule designated by an asterisk, such as NO_2^*, is [29]_____ _____. An atmospheric species designated with a dot, such as $HO\cdot$, is a [30]_____ possessing an [31]_____. An electron in an orbital of a molecule promoted to a higher energy level, but still retaining a spin opposite that of its former partner gives a molecule in an [32]_____ _____ state. As applied to photochemistry, the term $h\nu$ is the product of [33]_____ and [34]_____ and is equal to [35]_____. Having absorbed energy from a photon of electromagnetic radiation, loss of energy by a reaction such as $O_2^* \rightarrow O + O$ is known as [36]_____ whereas loss of energy by the immediate emission of light is [37]_____. A region of the atmosphere that raises at night is the [38]_____ characterized by the presence of [39]_____. The reaction $H_3C\cdot + H_3C\cdot \rightarrow C_2H_6$ showing the combination of two [40]_____ is an example

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of a [41]_____. The single most important reactive intermediate species in atmospheric chemical processes is [42]_____ _____. A related species containing two oxygen atoms is [43]_____ _____. The atmosphere is normally at least slightly acidic because of the presence of a low level of [44]_____. More strongly acidic pollutant acids found in the atmosphere are [45]_____. The only water-soluble base present at significant levels in the atmosphere is [46]_____ _____. The reaction $O_2 + h\nu \rightarrow O + O$ is of particular importance in the stratosphere because it [47]_____ _____. The atmospheric "nonpollutant" species of most concern is [48]_____ because of its potential to cause [49]_____ _____.

Answers to Chapter Summary

1. $N_2 > O_2 > H_2O >$ argon $> CO_2$
2. troposphere
3. stratosphere
4. photochemical reactions
5. light photons
6. $h\nu$
7. ultraviolet radiation
8. photosynthesis
9. respiration
10. those shown in Figure 14.1
11. the pressure is so low that they travel long distances before colliding with any other species with which they can react
12. the very cold tropopause
13. 1.34×10^3 watts per square meter
14. conduction, convection, and radiation
15. 500 nanometers in the visible region
16. 500 nanometers
17. absorbing outgoing infrared radiation
18. the percentage of solar radiation reflected from Earth's surface
19. the movement of air masses, heat, wind, and transitions of water in the atmosphere
20. weather
21. temperature, clouds, winds, humidity, horizontal visibility, type and quantity of precipitation, and atmospheric pressure
22. climate
23. latent heat
24. temperature inversion
25. microclimate
26. photons of electromagnetic radiation
27. radicals
28. inorganic oxides, oxidants, reductants, organics, oxidized organic species, photochemically active species, acids, bases, salts, and unstable reactive species such as HO· radical

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29. an electronically excited molecule
30. free radical
31. unpaired electron
32. excited singlet
33. Planck's constant, *h*
34. the frequency of electromagnetic radiation, ν
35. the energy of a quantum of electromagnetic radiation
36. dissociation
37. fluorescence
38. ionosphere
39. ions
40. (methyl) radicals
41. chain-terminating reaction
42. the hydroxyl radical, $HO\cdot$
43. the hydroperoxyl radical, $HOO\cdot$
44. carbon dioxide
45. HNO_3 and H_2SO_4
46. ammonia, NH_3
47. leads to the formation of protective ozone
48. carbon dioxide
49. global warming

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QUESTIONS AND PROBLEMS

1. What phenomenon is responsible for the temperature maximum at the boundary of the stratosphere and the mesosphere?
2. What function does a third body serve in an atmospheric chemical reaction?
3. Why does the lower boundary of the ionosphere lift at night?
4. Considering the total number of electrons in NO_2, why might it be expected that the reaction of a free radical with NO_2 is a chain-terminating reaction?
5. The average atmospheric pressure at sea level is 1.012×10^6 dynes/m^2. The value of g (acceleration of gravity) at sea level is 980 cm/sec^2. What is the mass in kg of the column of air having a cross-sectional area of 1.00 cm^2 at the earth's

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surface and extending to the limits of the atmosphere? (Recall that the dyne is a unit of force, and force = mass × acceleration of gravity.)

6. Suppose that 22.4 liters of air at STP is used to burn 1.50 g of carbon to form CO_2, and that the gaseous product is adjusted to STP. What is the volume and the average molar mass of the resulting mixture?
7. If the pressure is 0.01 atm at an altitude of 38 km and 0.001 at 57 km, what is it at 19 km (ignoring temperature variations)?
8. Measured in μm, what are the lower wavelength limits of solar radiation reaching the earth; the wavelength at which maximum solar radiation reaches the earth; and the wavelength at which maximum energy is radiated back into space?
9. Of the species O, HO*•, NO_2*, H_3C•, and N^+, which could most readily revert to a nonreactive, "normal" species in total isolation?
10. Of the gases neon, sulfur dioxide, helium, oxygen, and nitrogen, which shows the most variation in its atmospheric concentration?
11. A 12.0-liter sample of air at 25˚C and 1.00 atm pressure was collected and dried. After drying, the volume of the sample was exactly 11.50 L. What was the percentage *by weight* of water in the original air sample?
12. The sunlight incident upon a 1 square meter area perpendicular to the line of transmission of the solar flux just above the earth's atmosphere provides energy at a rate most closely equivalent to: (a) that required to power a pocket calculator, (b) that required to provide a moderate level of lighting for a 40-person-capacity classroom illuminated with fluorescent lights, (c) that required to propel a 2500-pound automobile at 55 mph, (d) that required to power a 100-watt incandescent light bulb, (e) that required to heat a 40-person classroom to 70˚F when the outside temperature is -10˚F.
13. At an altitude of 50 km, the average atmospheric temperature is essentially 0˚C. What is the average number of air molecules per cubic centimeter of air at this altitude?
14. What is the distinction between chemiluminescence and luminescence caused when light is absorbed by a molecule or atom?
15. State two factors that make the stratosphere particularly important in terms of acting as a region where atmospheric trace contaminants are converted to other, chemically less reactive, forms.
16. What two chemical species are most generally responsible for the removal of hydroxyl radical from the unpolluted troposphere.
17. What is the distinction between the symbols * and • in discussing chemically active species in the atmosphere?
18. Explain the meaning of "$h\nu$" when it appears in an atmospheric chemical reaction. What does it have to do with the wavelength of electromagnetic

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radiation? What is its relationship to energy?

19. What is the most abundant hydrocarbon in the atmosphere? What is its significance in relation to pollutant formation in the atmosphere?
20. In terms of Earth's heat balance, what is the significance of the wavelengths of electromagnetic radiation by which Earth receives most of its energy and by which it loses the energy that it receives?
21. Look up the diameter of Earth. With that information, justify the statement that Earth's atmosphere is "tissue thin." What does this fact have to do with the vulnerability of Earth's atmosphere to human insult?
22. In what respect is the troposphere homogeneous in respect to composition? With respect to which important constituent is it definitely not homogeneous?
23. Chapter 2 discusses some important properties of water as they relate to heat absorbed and released by water in various states. Discuss what these properties have to do with Earth's climate.
24. What is the tropopause? What crucial protective function does it serve?
25. What is the value of the solar constant? If energy falling on Earth at the top of the atmosphere could be collected with 100% efficiency, estimate how many square meters of solar energy collector would be required to provide the energy needs of a medium-size house. Explain why only a small fraction of this energy could be utilized in practice.
26. After examining Figure 14.4, suggest a class of pollutants that might counteract the effects of greenhouse gases.
27. What is the distinction between wind and air currents? How might these phenomena be involved in air pollution?
28. List and discuss the factors that make the laboratory study of atmospheric chemical phenomena so difficult.
29. List one characteristic of all free radicals. What is a characteristic common to all ions? How are the processes leading to their formation similar?
30. Figure 14.12 shows an annual fluctuation in global CO_2 levels. What causes this fluctuation? Does it have any implications for the potential control of greenhouse warming?
31. Give a reaction that explains why NO_2 is a key species involved in air pollution and the formation of photochemical smog.
32. In the reaction $O + O_2 + M \rightarrow O_3 + M$, what is "M" and why is it important in some atmospheric processes? What would likely happen to O_3 if "M" were not present?

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Manahan, Stanley E. "INORGANIC AIR POLLUTANTS"
Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

15 INORGANIC AIR POLLUTANTS

15.1 INTRODUCTION

This chapter addresses inorganic air pollutants of various kinds, including gases and particles. Organic air pollutants and the photochemical smog formed from them are discussed in Chapter 16.

Inorganic air pollutants consist of many kinds of substances. Many solid and liquid substances may become particulate air contaminants. Another important class of inorganic air pollutants consists of oxides of carbon, sulfur, and nitrogen. Carbon monoxide is a directly toxic material that is fatal at relatively small doses. Carbon dioxide is a natural and essential constituent of the atmosphere, and it is required for plants to use during photosynthesis. However, CO_2 may turn out to be the most significant air pollutant of all because of its potential as a greenhouse gas that might cause devastating global warming. Oxides of sulfur and nitrogen are acid-forming gases that can cause acid precipitation. Several other inorganic air pollutants, such as ammonia, hydrogen chloride, and hydrogen sulfide are also discussed in this chapter.

A number of gaseous inorganic pollutants enter the atmosphere as the result of human activities. Those added in the greatest quantities are CO, SO_2, NO, and NO_2. (These quantities are relatively small compared with the amount of CO_2 in the atmosphere. The possible environmental effects of increased atmospheric CO_2 levels are discussed later in this chapter.) Other inorganic pollutant gases include NH_3, N_2O, N_2O_5, H_2S, Cl_2, HCl, and HF. Substantial quantities of some of these gases are added to the atmosphere each year by human activities. Globally, atmospheric emissions of carbon monoxide, sulfur oxides, and nitrogen are of the order of one to several hundred million tons per year.

As with most aspects of chemistry in the real world, it is somewhat artificial and arbitrary to divide air pollutants between the inorganic and organic realms. For example, inorganic NO_2 undergoes photodissociation to start the processes that convert organic vapors to aldehydes, oxidants, and other substances characteristic of photochemical smog. Oxidants generated in such smog convert inorganic SO_2 to much more-acidic sulfuric acid, the major contributor to acid precipitation. Numerous

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other examples could be cited to illustrate the interrelationships among air pollutants of various kinds.

15.2 PARTICLES IN THE ATMOSPHERE

Particles in the atmosphere, which range in size from about one-half millimeter (the size of sand or drizzle) down to molecular dimensions, are made up of an amazing variety of materials and discrete objects that may consist of either solids or liquid droplets (Table 15.1). **Particulates** is a term that has come to stand for particles in the atmosphere, although *particulate matter* or simply *particles*, is preferred usage. Particulate matter makes up the most visible and obvious form of air pollution. Atmospheric **aerosols** are solid or liquid particles smaller than 100 μm in diameter. Pollutant particles in the 0.001 to 10 μm range are commonly suspended in the air near sources of pollution, such as the urban atmosphere, industrial plants, highways, and power plants.

Table 15.1 Important Terms Describing Atmospheric Particles

Term	Meaning
Aerosol	Colloidal-sized atmospheric particle
Condensation aerosol	Formed by condensation of vapors or reactions of gases
Dispersion aerosol	Formed by grinding of solids, atomization of liquids, or dispersion of dusts
Fog	Term denoting high level of water droplets
Haze	Denotes decreased visibility due to the presence of particles
Mists	Liquid particles
Smoke	Particles formed by incomplete combustion of fuel

Very small, solid particles include carbon black, silver iodide, combustion nuclei, and sea-salt nuclei formed by the loss of water from droplets of seawater. Larger particles include cement dust, wind-blown soil dust, foundry dust, and pulverized coal. Liquid particulate matter, **mist**, includes raindrops, fog, and sulfuric acid droplets. Some particles are of biological origin, such as viruses, bacteria, bacterial spores, fungal spores, and pollen. Particulate matter may be organic or inorganic; both types are very important atmospheric contaminants.

Chemical Processes for Inorganic Particle Formation

Metal oxides constitute a major class of inorganic particles in the atmosphere. These are formed whenever fuels containing metals are burned. For example, particulate iron oxide is formed during the combustion of pyrite-containing coal:

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$$3FeS_2 + 8O_2 \rightarrow Fe_3O_4 + 6SO_2 \quad (15.2.1)$$

Organic vanadium in residual fuel oil is converted to particulate vanadium oxide. Part of the calcium carbonate in the ash fraction of coal is converted to calcium oxide and is emitted to the atmosphere through the stack:

$$CaCO_3 + \text{heat} \rightarrow CaO + CO_2 \quad (15.2.2)$$

A common process for the formation of aerosol mists involves the oxidation of atmospheric sulfur dioxide to sulfuric acid, a hygroscopic substance that accumulates atmospheric water to form small liquid droplets:

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \quad (15.2.3)$$

When basic air pollutants, such as ammonia or calcium oxide, are present, they react with sulfuric acid to form salts:

$$H_2SO_4(\text{droplet}) + 2NH_3(g) \rightarrow (NH_4)_2SO_4\ (\text{droplet}) \quad (15.2.4)$$

$$H_2SO_4(\text{droplet}) + CaO(s) \rightarrow CaSO_4(\ \text{droplet}) \quad (15.2.5)$$

Under low-humidity conditions, water is lost from these droplets and a solid salt aerosol is formed.

The preceding examples show several ways in which solid or liquid inorganic aerosols are formed by chemical reactions. Such reactions constitute an important general process for the formation of aerosols, particularly the smaller particles.

15.3 THE COMPOSITION OF INORGANIC PARTICLES

Figure 15.1 illustrates the basic factors responsible for the composition of inorganic particulate matter. In general, the proportions of elements in atmospheric particulate matter reflect relative abundances of elements in the parent material. The source of particulate matter is reflected in its elemental composition, taking into consideration chemical reactions that may change the composition. For example, particulate matter largely from ocean spray origin in a coastal area receiving sulfur dioxide pollution may show anomalously high sulfate and corresponding low chloride content. The sulfate comes from atmospheric oxidation of sulfur dioxide to form nonvolatile ionic sulfate, whereas some chloride originally from the NaCl in the seawater may be lost from the solid aerosol as volatile HCl:

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \quad (15.3.1)$$

$$H_2SO_4 + 2NaCl(\text{particulate}) \rightarrow Na_2SO_4(\text{particulate}) + 2HCl \quad (15.3.2)$$

The chemical composition of atmospheric particulate matter is quite diverse. Among the constituents of inorganic particulate matter found in polluted atmospheres are salts, oxides, nitrogen compounds, sulfur compounds, various metals, and radionuclides. In coastal areas, sodium and chlorine get into atmospheric par-

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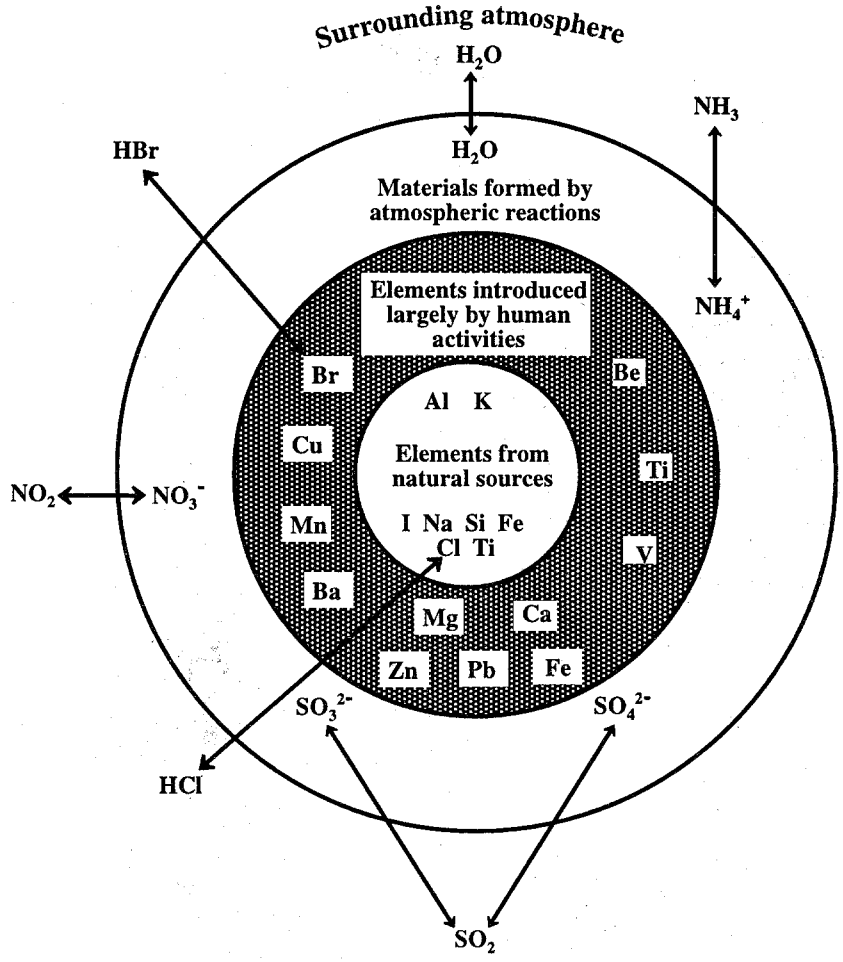


Figure 15.1 Some of the components of inorganic particulate matter and their origins.

ticles as sodium chloride from sea spray. The major trace elements that typically occur at levels above 1 μg/m^3 in particulate matter are aluminum, calcium, carbon, iron, potassium, sodium, and silicon; note that most of these tend to originate from terrestrial sources. Lesser quantities of copper, lead, titanium, and zinc, and even lower levels of antimony, beryllium, bismuth, cadmium, cobalt, chromium, cesium, lithium, manganese, nickel, rubidium, selenium, strontium, and vanadium are commonly observed. The likely sources of some of these elements are given below:

- **Al, Fe, Ca, Si**: Soil erosion, rock dust, coal combustion
- **C**: Incomplete combustion of carbonaceous fuels
- **Na, Cl**: Marine aerosols, chloride from incineration of organohalide polymer wastes

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- **Sb, Se**: Very volatile elements, possibly from the combustion of oil, coal, or refuse
- **V**: Combustion of residual petroleum (present at very high levels in residues from Venezuelan crude oil)
- **Zn**: Tends to occur in small particles, probably from combustion
- **Pb**: Combustion of leaded fuels and wastes containing lead

Particulate carbon as soot, carbon black, coke, and graphite originates from auto and truck exhausts, heating furnaces, incinerators, power plants, and steel and foundry operations, and composes one of the more visible and troublesome particulate air pollutants. Because of its good adsorbent properties, carbon can be a carrier of gaseous and other particulate pollutants. Particulate carbon surfaces may catalyze some heterogeneous atmospheric reactions, including the important conversion of SO_2 to sulfate.

Fly Ash

Much of the mineral particulate matter in a polluted atmosphere is in the form of oxides and other compounds produced during the combustion of high-ash fossil fuel. Much of the mineral matter in fossil fuels such as coal or lignite is converted during combustion to a fused, glassy, bottom ash that presents no air pollution problems. Smaller particles of **fly ash** enter furnace flues and are efficiently collected in a properly equipped stack system. However, some fly ash escapes through the stack and enters the atmosphere. Unfortunately, the fly ash thus released tends to consist of smaller particles, which do the most damage to human health, plants, and visibility.

The composition of fly ash varies widely, depending upon the source of fuel. The predominant constituents are oxides of aluminum, calcium, iron, and silicon. Other elements that occur in fly ash are magnesium, sulfur, titanium, phosphorus, potassium, and sodium. Elemental carbon (soot, carbon black) is a significant fly ash constituent.

Asbestos

Asbestos is the name given to a group of fibrous silicate minerals, typically those of the serpentine group, for which the approximate formula is $Mg_3P(Si_2O_5)(OH)_4$. The tensile strength, flexibility, and nonflammability of asbestos have led to many uses in the past including structural materials, brake linings, insulation, and pipe manufacture.

Asbestos is of concern as an air pollutant because, when inhaled, it can cause asbestosis (a pneumonia condition), mesothelioma (tumor of the mesothelial tissue lining the chest cavity adjacent to the lungs), and bronchogenic carcinoma (cancer originating with the air passages in the lungs). Therefore, uses of asbestos have been severely curtailed and widespread programs have been undertaken to remove the material from buildings.

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Toxic Metals

Some of the metals found predominantly as particulate matter in polluted atmospheres are known to be hazardous to human health. All of these except beryllium are so-called "heavy metals." Lead is the toxic metal of greatest concern in the urban atmosphere because it comes closest to being present at a toxic level; mercury ranks second. Others include beryllium, cadmium, chromium, vanadium, nickel, and arsenic (a metalloid).

Atmospheric mercury is of concern because of its toxicity, volatility, and mobility. Some atmospheric mercury is associated with particulate matter. Much of the mercury entering the atmosphere does so as volatile elemental mercury from coal combustion and volcanoes. Volatile organomercury compounds, such as dimethylmercury, $(CH_3)_2Hg$, and monomethylmercury salts, such as $(CH_3)HgBr$, are also encountered in the atmosphere.

With the reduction of leaded fuels, atmospheric lead is of less concern than it used to be. However, during the decades that leaded gasoline containing tetraethyllead was the predominant automotive fuel, particulate lead halides were emitted in large quantities. Lead halides are emitted from engines burning leaded gasoline through the action of dichlorethane and dibromoethane added as halogenated scavengers to form volatile lead chloride, lead bromide, and lead chlorobromide, thereby preventing the accumulation of lead oxides inside engines.

Beryllium is used for the formulation of specialty alloys employed in electrical equipment, electronic instrumentation, space gear, and nuclear reactor components, so that distribution of beryllium is by no means comparable to that of other toxic metals such as lead or mercury. However, because of its "high tech" applications, consumption of beryllium may increase in the future. Because of its high toxicity, beryllium has the lowest allowable limit in the atmosphere of all the elements. One of the main results resulting from the recognition of beryllium toxicity hazards was the elimination of this element from phosphors (coatings that produce visible light from ultraviolet light) in fluorescent lamps.

Radioactive Particles

A significant natural source of radionuclides in the atmosphere is **radon**, a noble gas product of radium decay. Radon may enter the atmosphere as either of two isotopes, ^{222}Rn (half-life 3.8 days) and ^{220}Rn (half-life 54.5 seconds). Both are alpha emitters in decay chains that terminate with stable isotopes of lead. The initial decay products, ^{218}Po and ^{216}Po, are nongaseous and adhere readily to atmospheric particulate matter. Therefore, some of the radioactivity detected in these particles is of natural origin. Furthermore, cosmic rays act on nuclei in the atmosphere, reacting to produce other radionuclides, including ^{7}Be, ^{10}Be, ^{14}C, ^{39}Cl, ^{3}H, ^{22}Na, ^{32}P, and ^{33}P.

The combustion of fossil fuels introduces radioactivity into the atmosphere in the form of radionuclides contained in fly ash. Large coal-fired power plants lacking ash-control equipment can introduce up to several hundred milliCuries of radionuclides into the atmosphere each year, far more than either an equivalent nuclear or oil-fired power plant.

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The above-ground detonation of nuclear weapons, which hopefully will not ever occur again, can add large amounts of radioactive particulate matter to the atmosphere. Among the radioisotopes that can be detected in rainfall falling after atmospheric nuclear weapon detonation are ^{91}Y, ^{141}Ce, ^{144}Ce, ^{147}Nd, ^{147}Pm, ^{149}Pm, ^{151}Sm, ^{153}Sm, ^{155}Eu, ^{156}Eu, ^{89}Sr, ^{90}Sr, ^{115m}Cd, ^{129m}Te, ^{131}I, ^{132}Te, and ^{140}Ba. (Note that "m" denotes a metastable state that decays by gamma-ray emission to an isotope of the same element.)

15.4 EFFECTS OF PARTICLES

Atmospheric particles have numerous effects. The most obvious of these is reduction and distortion of visibility. Particles provide active surfaces upon which heterogeneous atmospheric chemical reactions can occur and nucleation bodies for the condensation of atmospheric water vapor, thereby exerting a significant influence upon weather and air pollution phenomena. Some chemical and physical aspects of atmospheric particles are illustrated in Figure 15.2.

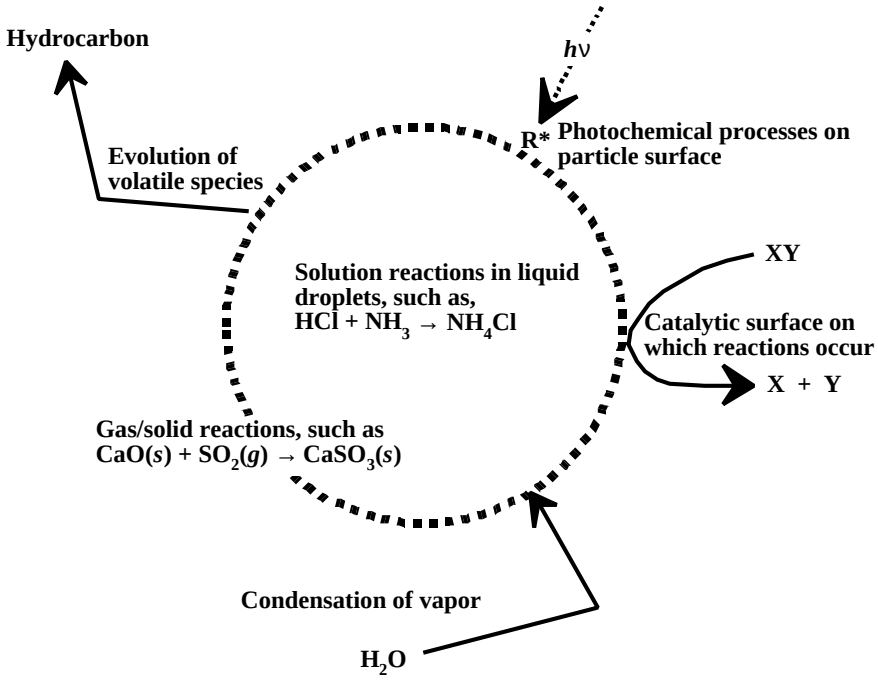


Figure 15.2 Aspects of particle reactions and effects in the atmosphere.

The most visible influence that aerosol particles have upon air quality results from optical effects. Particles smaller than about 0.1 μm in diameter scatter light much like molecules, that is, Rayleigh scattering. Generally, such particles have an insignificant effect upon visibility in the atmosphere. The light-scattering and intercepting properties of particles larger than 1 μm are approximately proportional to the particle's cross-sectional area. Particles of 0.1 μm–1 μm cause interference phenomena because they are about the same dimensions as the wavelengths of visible light, so their light-

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scattering properties are especially significant.

Atmospheric particles inhaled through the respiratory tract may damage health. Relatively large particles are mostly retained in the nasal cavity and in the pharynx, whereas very small particles are likely to reach the lungs and be retained by them. The respiratory system possesses mechanisms for the expulsion of inhaled particles. In the ciliated region of the respiratory system, particles are carried as far as the entrance to the gastrointestinal tract by a flow of mucus. Macrophages in the nonciliated pulmonary regions carry particles to the ciliated region.

The respiratory system may be damaged directly by particulate matter that enters the blood system or lymph system through the lungs. In addition, soluble components of the particulate matter may be transported to organs some distance from the lungs and have a detrimental effect on these organs. Particles cleared from the respiratory tract are largely swallowed into the gastrointestinal tract.

A strong correlation has been found between increases in the daily mortality rate and acute episodes of air pollution. In such cases, high levels of particulate matter are accompanied by elevated concentrations of SO_2 and other pollutants, so that any conclusions must be drawn with caution.

15.5 CONTROL OF PARTICULATE EMISSIONS

The removal of particulate matter from gas streams is the most widely practiced means of air pollution control. A number of devices that differ widely in effectiveness, complexity, and cost have been developed for this purpose. The selection of a particle removal system for a gaseous waste stream depends upon the particle loading, nature of particles (size distribution), and type of gas scrubbing system used.

Particle Removal by Sedimentation and Inertia

The simplest means of particulate matter removal is **sedimentation**, a phenomenon that occurs continuously in nature. Gravitational settling chambers can be employed for the removal of particles from gas streams by simply settling under the influence of gravity. These chambers take up large amounts of space and have low collection efficiencies, particularly for small particles.

Gravitational settling of particles is enhanced by increased particle size, which occurs spontaneously by coagulation. Thus, over time, the size of particles increases and the number of particles decreases in a mass of air that contains particles. Brownian motion of particles less than about 0.1 μm in size is primarily responsible for their contact, enabling coagulation to occur. Particles greater than about 0.3 μm in radius do not diffuse appreciably and serve primarily as receptors of smaller particles.

Inertial mechanisms used for particle removal depend upon the fact that the radius of the path of a particle in a rapidly moving, curving air stream is larger than the path of the stream as a whole. Therefore, when a gas stream is spun by vanes, a fan, or a tangential gas inlet, the particulate matter may be collected on a separator wall because the particles are forced outward by centrifugal force. Devices utilizing this mode of operation are called **dry centrifugal collectors**.

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Particle filtration

Fabric filters, as their name implies, consist of fabrics that allow the passage of gas but retain particulate matter. These are used to collect dust in bags contained in structures called *baghouses*. Periodically, the fabric composing the filter is shaken to remove the particles and to reduce back-pressure to acceptable levels. Typically, the bag is in a tubular configuration, as shown in Figure 15.3. Numerous other configurations are possible. Collected particulate matter is removed from bags by mechanical agitation, blowing air on the fabric, or rapid expansion and contraction of the bags.

Although simple, baghouses are generally effective in removing particles from exhaust gas. Particles as small as 0.01 μm in diameter are removed, and removal efficiency is relatively high for particles down to 0.5 μm in diameter.

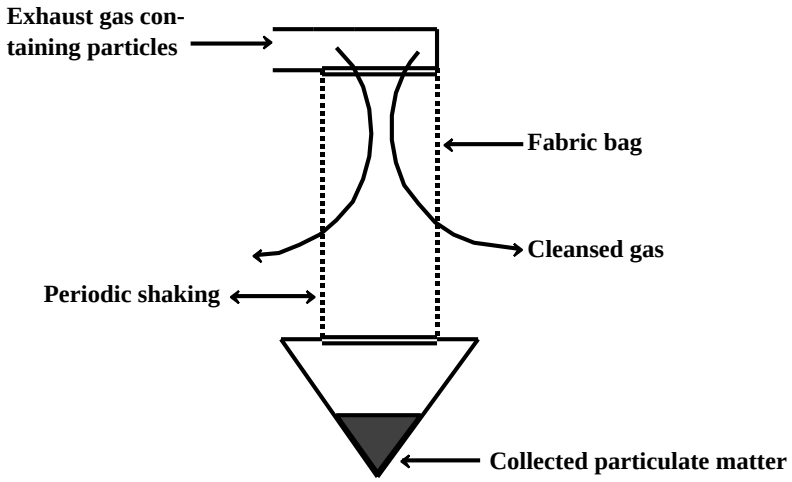


Figure 15.3 Baghouse collection of particulate emissions.

Scrubbers

A venturi scrubber passes gas through a converging section, throat, and diverging section as shown in Figure 15.4. Injection of the scrubbing liquid at right angles to incoming gas breaks the liquid into very small droplets, which are ideal for scavenging particles from the gas stream. In the reduced-pressure (expanding) region of the venturi, some condensation can occur, adding to the scrubbing efficiency. In addition to removing particles, venturis can serve as quenchers to cool exhaust gas and as scrubbers for pollutant gases.

Electrostatic Removal

Aerosol particles may acquire electrical charges. In an electric field, such particles are subjected to a force, F (dynes) given by

$$F = eq \tag{15.5.1}$$

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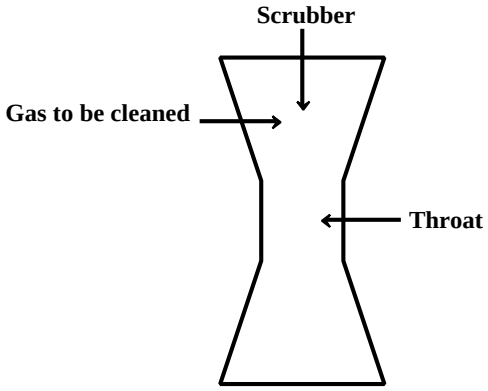


Figure 15.4 Venturi scrubber.

where E is the voltage gradient (statvolt/cm) and q is the electrostatic charge charge on the particle (in esu). This phenomenon has been widely used in highly efficient **electrostatic precipitators**, as shown in Figure 15.5. The particles acquire a charge when the gas stream is passed through a high-voltage, direct-current corona. Because of the charge, the particles are attracted to a grounded surface, from which they may be later removed. Ozone may be produced by the corona discharge. Similar devices used as household dust collectors may produce toxic oxone if not operated properly.

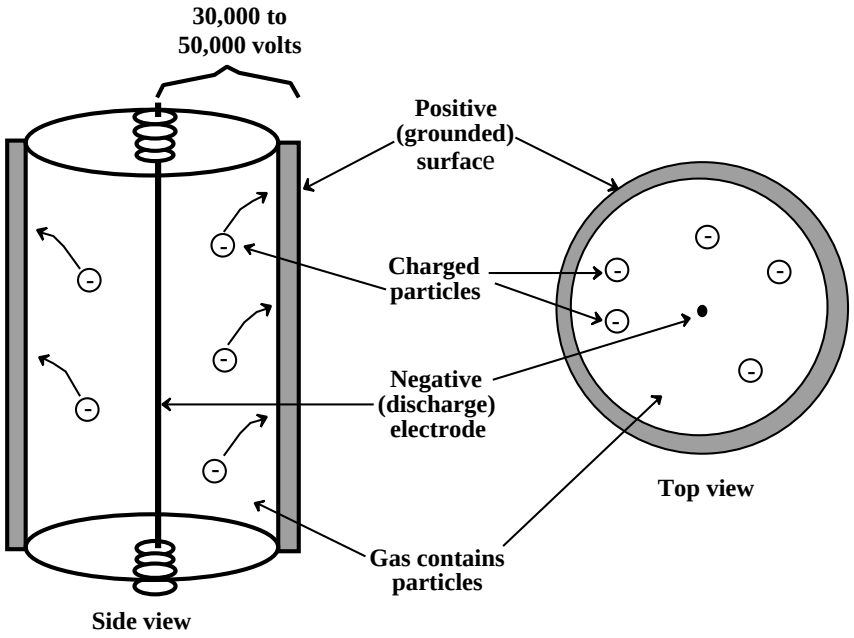


Figure 15.5 Schematic diagram of an electrostatic precipitator.

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15.6 CARBON OXIDES

Carbon Monoxide

Carbon monoxide, CO, causes problems in cases of locally high concentrations. The toxicity of carbon monoxide is discussed in Chapter 23. The overall atmospheric concentration of carbon monoxide is about 0.1 ppm. Much of this CO is present as an intermediate in the oxidation of methane by hydroxyl radical. Because of carbon monoxide emissions from internal combustion engines, highest levels of this toxic gas tend to occur in congested urban areas at times when the maximum number of people are exposed, such as during rush hours. At such times, carbon monoxide levels in the atmosphere have become as high as 50–100 ppm. Automotive air pollution control devices have reduced these levels significantly during the last 25 years.

Control of Carbon Monoxide Emissions

Since the internal combustion engine is the primary source of localized pollutant carbon monoxide emissions, control measures have been concentrated on the automobile. Carbon monoxide emissions may be lowered by employing a leaner air-fuel mixture, that is, one in which the weight ratio of air to fuel is relatively high. At air-fuel(weight:weight) ratios exceeding approximately 16:1, an internal combustion engine emits virtually no carbon monoxide. Modern automobiles use catalytic exhaust reactors and precise computerized control of engine operation to cut down on carbon monoxide emissions.

Fate of Atmospheric CO

The residence time of carbon monoxide in the atmosphere is of the order of 4 months. It is generally agreed that carbon monoxide is removed from the atmosphere by reaction with hydroxyl radical, $HO^{\bullet}$:

$$CO + HO^{\bullet} \rightarrow CO_2 + H \qquad (15.6.1)$$

The reaction produces hydroperoxyl radical as a product:

$$O_2 + H + M \rightarrow HOO^{\bullet} + M \quad (M \text{ is an energy-absorbing third body, usually a molecule of } O_2 \text{ or } N_2) \qquad (15.6.2)$$

$HO^{\bullet}$ is regenerated from $HOO^{\bullet}$ by the following reactions:

$$HOO^{\bullet} + NO \rightarrow HO^{\bullet} + NO_2 \qquad (15.6.3)$$

$$HOO^{\bullet} + HOO^{\bullet} \rightarrow H_2O_2 \qquad (15.6.4)$$

The latter reaction is followed by photochemical dissociation of H_2O_2 to regenerate $HO^{\bullet}$:

$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \qquad (15.6.5)$$

Methane is also involved through the atmospheric CO-$HO^{\bullet}$-CH_4 cycle.

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Soil microorganisms act to remove CO from the atmosphere. Therefore, soil is a sink for carbon monoxide.

Carbon Dioxide and Global Warming

Carbon dioxide and other infrared-absorbing trace gases in the atmosphere contribute to global warming—the "greenhouse effect"—by allowing incoming solar radiant energy to penetrate to the Earth's surface while reabsorbing infrared radiation emanating from it. Levels of these "greenhouse gases" have increased at a rapid rate during recent decades and are continuing to do so. Concern over this phenomenon has intensified since about 1980. This is because the 1990s have been the warmest 10-year period recorded since accurate temperature records have been kept. Prior to that time the 1980s were the warmest decade on record. In March 2000 the U.S. National Climatic Data Center announced that the 1999-2000 winter in the 48 contiguous United States was the warmest on record, with an average winter temperature of 3.6˚C. The two preceding winters had also set records of 3.2˚C for the 1998-1999 winter and 3.1˚C for the 1997-1998 winter. During the 1999-2000 winter both the first freeze and first snowfall came later than ever in colder regions of the 48 states, including New England and the Northern Plains. Numerous places across the northern tier of states set high temperature records during February 2000. The spring of 2000 was the warmest ever recorded in the United States. Figure 15.6 shows trends in global temperature over the last century.

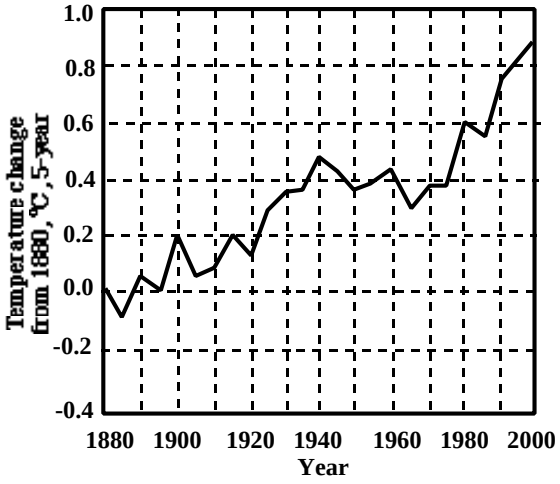


Figure 15.6 Trends in global temperature over the last century.

There are many uncertainties surrounding the issue of greenhouse warming. However, it is known that CO_2 and other greenhouse gases, such as CH_4, absorb infrared radiation by which Earth loses heat. The levels of these gases have increased markedly since about 1850, as nations have become industrialized and as forest lands and grasslands have been converted to agriculture. Chlorofluorocarbons, which also are greenhouse gases, were not even introduced into the atmosphere until the 1930s. Although trends in levels of these gases are well known, their effects on global

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temperature and climate are much less certain. The phenomenon has been the subject of much computer modeling. Most models predict global warming of 1.5–5˚C, about as much again as has occurred since the last ice age. Such warming would have profound effects on rainfall, plant growth, and sea levels, which might rise as much as 0.5–1.5 meters.

Carbon dioxide is the gas most commonly thought of as a greenhouse gas; it is responsible for about half of the atmospheric heat retained by trace gases. It is produced primarily by burning of fossil fuels and deforestation accompanied by burning and biodegradation of biomass. On a molecule-for-molecule basis, methane, CH_4, is 20–30 times more effective in trapping heat than is CO_2. Other trace gases that contribute are chlorofluorocarbons and N_2O.

Analyses of gases trapped in polar ice samples indicate that pre-industrial levels of CO_2 and CH_4 in the atmosphere were approximately 260 parts per million and 0.70 ppm, respectively. Over the last 300 years, these levels have increased to current values of around 360 ppm, and l.8 ppm, respectively; most of the increase by far has taken place at an accelerating pace over the last 100 years. (A note of interest is the observation based upon analyses of gases trapped in ice cores that the atmospheric level of CO_2 at the peak of the last ice age about 18,000 years past was 25 percent *below* preindustrial levels.) About half of the increase in carbon dioxide in the last 300 years can be attributed to deforestation, which still accounts for approximately 20 % of the annual increase in this gas. Carbon dioxide is increasing by about 1 ppm per year. Methane is going up at a rate of almost 0.02 ppm/year. The comparatively very rapid increase in methane levels is attributed to a number of factors resulting from human activities. Among these are direct leakage of natural gas, byproduct emissions from coal mining and petroleum recovery, and release from the burning of savannas and tropical forests. Biogenic sources resulting from human activities produce large amounts of atmospheric methane. These include methane from bacteria degrading organic matter, such as municipal refuse in landfills; methane evolved from anaerobic biodegradation of organic matter in rice paddies; and methane emitted as the result of bacterial action in the digestive tracts of ruminant animals.

The steady increase in global carbon dioxide levels is shown in Figure 15.7, which also shows a seasonal cycle in carbon dioxide levels in the northern hemisphere. Maximum values occur in April and minimum values in late September or October. These oscillations are due to the “photosynthetic pulse,” influenced most strongly by forests in middle latitudes. Forests have a much greater influence than other vegetation because trees carry out more photosynthesis. Furthermore, forests store enough fixed but readily oxidizable carbon in the form of wood and humus to have a marked influence on atmospheric CO_2 content. Thus, during the summer months, forest trees carry out enough photosynthesis to reduce the atmospheric carbon dioxide content markedly. During the winter, metabolism of biota, such as bacterial decay of humus, releases a significant amount of CO_2. Therefore, the current worldwide destruction of forests and conversion of forest lands to agricultural uses contributes substantially to a greater overall increase in atmospheric CO_2 levels.

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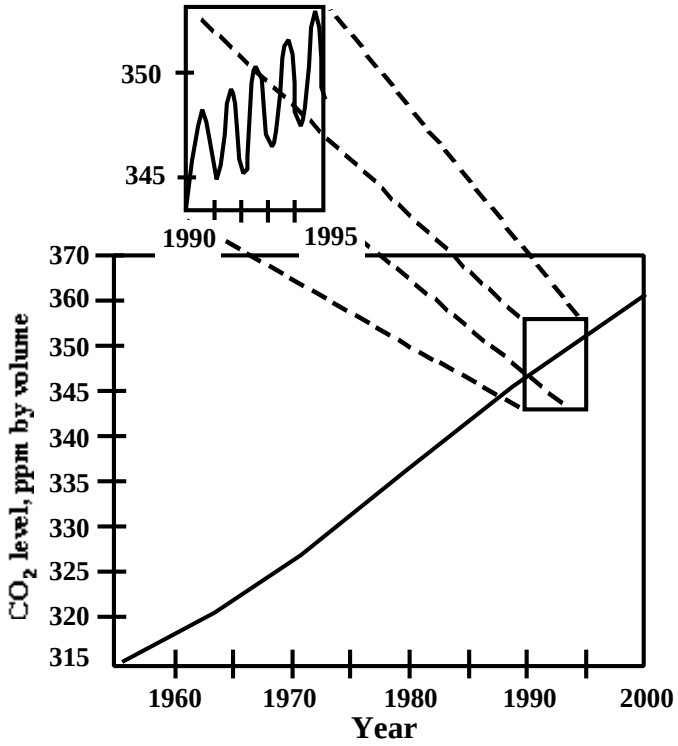


Figure 15.7 Increases in atmospheric CO_2 levels in recent years. The inset illustrates seasonal variations in the Northern Hemisphere.

Both positive and negative feedback mechanisms may be involved in determining the rates at which carbon dioxide and methane build up in the atmosphere. Laboratory studies indicate that increased CO_2 levels in the atmosphere cause accelerated uptake of this gas by plants undergoing photosynthesis, which tends to slow buildup of atmospheric CO_2. Given adequate rainfall, plants living in a warmer climate that would result from the greenhouse effect would grow faster and take up more CO_2. This could be an especially significant effect of forests, which have a high CO_2-fixing ability. However, the projected rate of increase in carbon dioxide levels is so rapid that forests would lag behind in their ability to fix additional CO_2. Similarly, higher atmospheric CO_2 concentrations will result in accelerated sorption of the gas by oceans. The amount of dissolved CO_2 in the oceans is about 60 times the amount of CO_2 gas in the atmosphere. However, the times for transfer of carbon dioxide from the atmosphere to the top layers of the ocean are of the order of years. Because of low mixing rates, the times for transfer of carbon dioxide from the upper approximately 100-meter layer of the oceans to ocean depths is much longer, of the order of decades. Therefore, like the uptake of CO_2 by forests, increased absorption by oceans will lag behind the emissions of CO_2. Severe drought conditions resulting from climatic warming could cut down substantially on CO_2 uptake by plants. Warmer conditions would accelerate release of both CO_2 and CH_4 by microbial degradation of organic matter. (It is important to realize that about twice as much carbon is held in soil in dead organic matter— necrocarbon—potentially degradable

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to CO_2 and CH_4 as is present in the atmosphere.) Global warming might speed up the rates at which biodegradation adds these gases to the atmosphere.

Carbon dioxide levels will continue to increase at a rate dependent upon future levels of CO_2 production and the fraction of that production that remains in the atmosphere. Given plausible projections of CO_2 production and a reasonable estimate that half of that amount will remain in the atmosphere, projections can be made that indicate that sometime during the middle part of the next century the concentration of this gas will reach 600 ppm in the atmosphere. This is well over twice the levels estimated for pre-industrial times. Much less certain are the effects that this change will have on climate. It is virtually impossible for the elaborate computer models used to estimate these effects to accurately take account of all variables, such as the degree and nature of cloud cover. Clouds both reflect incoming light radiation and absorb outgoing infrared radiation, with the former effect tending to predominate. The magnitudes of these effects depend upon the degree of cloud cover, brightness, altitude, and thickness. In the case of clouds, too, feedback phenomena occur; for example, warming induces formation of more clouds, which reflect more incoming energy. Most computer models predict global warming of at least 3.0˚C and as much as 5.5˚C occurring over a period of just a few decades. These estimates are sobering because they correspond to the approximate temperature increase since the last ice age 18,000 years past, which took place at a much slower pace of only about 1 or 2˚C per 1,000 years.

Drought is one of the most serious problems that could arise from major climatic change resulting from greenhouse warming. Typically, a 3-degree warming would be accompanied by a 10 % decrease in precipitation. Water shortages would be aggravated, not just from decreased rainfall, but from increased evaporation, as well. Increased evaporation results in decreased runoff, thereby reducing water available for agricultural, municipal, and industrial use. Water shortages, in turn, lead to increased demand for irrigation and to the production of lower quality, higher salinity runoff water and wastewater. In the U. S., such a problem would be especially intense in the Colorado River basin, which supplies much of the water used in the rapidly growing U.S. Southwest.

A variety of other problems, some of them unforeseen as of now, could result from global warming. An example is the effect of warming on plant and animal pests — insects, weeds, diseases, and rodents. Many of these would certainly thrive much better under warmer conditions.

Interestingly, another air pollutant, acid-rain-forming sulfur dioxide (see Section 15.7), may have a counteracting effect on greenhouse gases. This is because sulfur dioxide is oxidized in the atmosphere to sulfuric acid, forming a light-reflecting haze. Furthermore, the sulfuric acid and resulting sulfates act as condensation nuclei (Section 14.5) that increases the extent, density, and brightness of light-reflecting cloud cover.

Chemically and photochemically, carbon dioxide is a comparatively insignificant species because of its relatively low concentrations and low photochemical reactivity. The one significant photochemical reaction that carbon dioxide undergoes, and a major source of CO at higher altitudes, is the photodissociation of CO_2 by energetic solar ultraviolet radiation in the stratosphere:

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$$CO_2 + h\nu \rightarrow CO + O \qquad (15.6.6)$$

15.7 SULFUR DIOXIDE SOURCES AND THE SULFUR CYCLE

Figure 15.8 shows the main aspects of the global sulfur cycle. This cycle involves primarily H_2S, $(CH_3)_2S$, SO_2, SO_3, and sulfates. There are many uncertainties regarding the sources, reactions, and fates of these atmospheric sulfur species. Approximately 100 million metric tons of sulfur per year enter the global atmosphere through anthropogenic activities, primarily as SO_2 from the combustion of coal and residual fuel oil. The greatest uncertainties in the cycle have to do with nonanthropogenic sulfur, which enters the atmosphere largely as SO_2 and H_2S from volcanoes, and as $(CH_3)_2S$ and H_2S from the biological decay of organic matter and reduction of sulfate. The single largest source of natural sulfur discharged to the atmosphere is now believed to be biogenic dimethyl sulfide, $(CH_3)_2S$, from marine sources. Any H_2S that does get into the atmosphere is converted rapidly to SO_2 by the following overall process:

$$H_2S + {}^3\!/_2 O_2 \rightarrow SO_2 + H_2O \qquad (15.7.1)$$

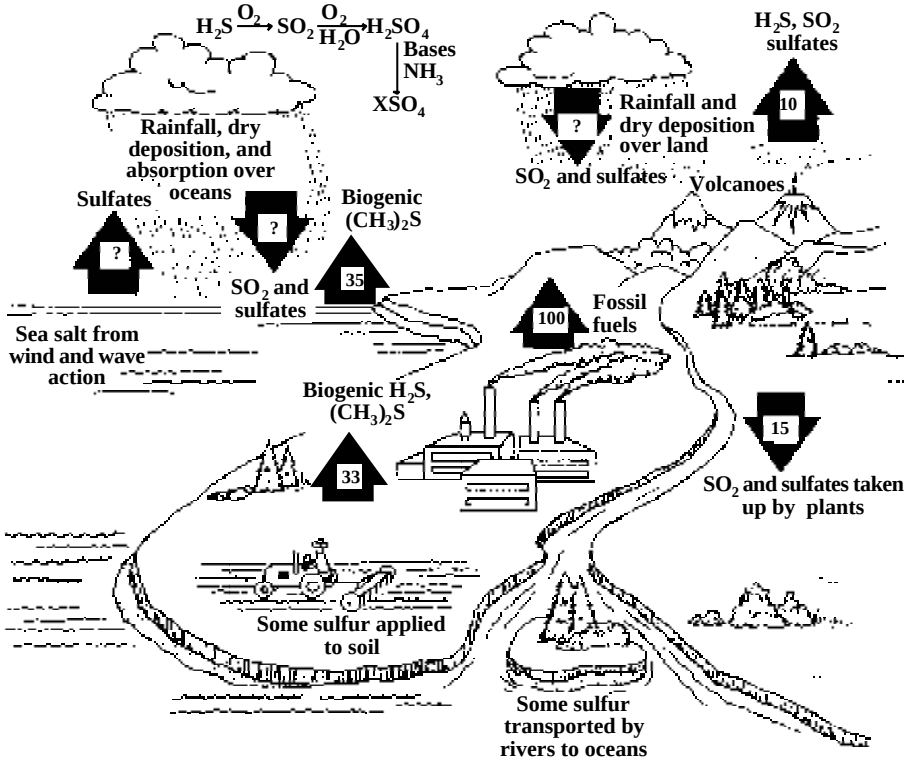


Figure 15.8 The global atmospheric sulfur cycle. Fluxes of sulfur represented by the arrows are in millions of metric tons per year. Those marked with a question mark are uncertain, but large, probably of the order of 100 million metric tons per year.

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The initial reaction is hydrogen ion abstraction by hydroxyl radical, followed by two other reactions to give SO_2:

$$H_2S + HO\bullet \rightarrow HS\bullet + H_2O \quad (15.7.2)$$

$$HS\bullet + O_2 \rightarrow HO\bullet + SO \quad (15.7.3)$$

$$SO + O_2 \rightarrow SO_2 + O \quad (15.7.4)$$

The primary source of anthropogenic sulfur dioxide is coal, from which sulfur must be removed at great expense to keep sulfur dioxide emissions at acceptable levels. Approximately half of the sulfur in coal is in some form of pyrite, FeS_2, and the other half is organic sulfur. The production of sulfur dioxide by the combustion of pyrite is given by the following reaction:

$$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2 \quad (15.7.5)$$

Sulfur Dioxide Reactions in the Atmosphere

Many factors, including temperature, humidity, light intensity, atmospheric transport, and surface characteristics of particulate matter, can influence the atmospheric chemical reactions of sulfur dioxide. Like many other gaseous pollutants, sulfur dioxide undergoes chemical reactions resulting in the formation of particulate matter. Whatever the processes involved, much of the sulfur dioxide in the atmosphere ultimately is oxidized to sulfuric acid and sulfate salts, particularly ammonium sulfate and ammonium hydrogen sulfate.

Effects of Atmospheric Sulfur Dioxide

Atmospheric sulfur dioxide's primary health effect is upon the respiratory tract, producing irritation and increasing airway resistance, especially to people with respiratory weaknesses and sensitized asthmatics. Increased effort to breathe and stimulated mucus secretion may occur with sulfur dioxide inhalation in air.

Acute exposure to high levels of atmospheric sulfur dioxide kills leaf tissue (leaf necrosis). The edges of the leaves and the areas between the leaf veins are particularly damaged. Chronic exposure of plants to sulfur dioxide causes chlorosis, a bleaching or yellowing of green leaves. Sulfur dioxide in the atmosphere is converted to sulfuric acid, so that in areas with high levels of sulfur dioxide pollution, plants may be damaged by sulfuric acid aerosols. Such damage appears as small spots where sulfuric acid droplets have impinged on leaves.

Sulfur Dioxide Removal

A number of processes are being used to remove sulfur and sulfur oxides from fuel before combustion and from stack gas after combustion. Most of these efforts concentrate on coal, since it is the major source of sulfur oxides pollution. Physical separation techniques can be used to remove discrete particles of pyritic sulfur from coal. Chemical methods can also be employed for removal of sulfur from coal. Fluidized bed combustion of coal promises to eliminate SO_2 emissions at the point of combustion. The process consists of burning granular coal in a bed of finely divided

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limestone or dolomite maintained in a fluid-like condition by air injection. Heat calcines the limestone,

$$CaCO_3 \rightarrow CaO + CO_2 \quad (15.7.6)$$

and the lime produced absorbs SO_2:

$$CaO + SO_2 \ (+ \tfrac{1}{2}O_2) \rightarrow CaSO_3 \ (CaSO_4) \quad (15.7.7)$$

Many processes have been proposed or studied for the removal of sulfur dioxide from stack gas. Table 15.2 summarizes major stack gas scrubbing systems. These include throwaway and recovery systems as well as wet and dry systems.

Current practice with lime and limestone scrubber systems often injects slurry into the scrubber loop beyond the boilers. These scrubbers can remove well over 90% of both SO_2 and fly ash when operating properly. In addition to corrosion and scaling problems, disposal of lime sludge poses formidable obstacles. The quantity of this sludge may be appreciated by considering that approximately 1 ton of limestone is required for each 5 tons of coal.

Recovery systems in which sulfur dioxide or elemental sulfur are removed from the spent sorbing material, which is recycled, are much more desirable from an environmental viewpoint than are throwaway systems. Many kinds of recovery processes have been investigated, including those that involve scrubbing with magnesium oxide slurry, sodium sulfite solution, ammonia solution, or sodium citrate solution.

Sulfur dioxide trapped in a stack-gas-scrubbing process can be converted to hydrogen sulfide by reaction with synthesis gas (H_2, CO, CH_4),

$$SO_2 + (H_2, CO, CH_4) \leftarrow\rightarrow H_2S + CO_2 \quad (15.7.8)$$

The Claus reaction is then employed to produce elemental sulfur:

$$2H_2S + SO_2 \leftarrow\rightarrow 2H_2O + 3S \quad (15.7.9)$$

15.8 NITROGEN OXIDES IN THE ATMOSPHERE

The three oxides of nitrogen normally encountered in the atmosphere are nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2). Microbially generated nitrous oxide is relatively unreactive and probably does not significantly influence important chemical reactions in the lower atmosphere. Its levels decrease rapidly with altitude in the stratosphere due to the photochemical reaction

$$N_2O + h\nu \rightarrow N_2 + O \quad (15.8.1)$$

and some reaction with singlet atomic oxygen:

$$N_2O + O \rightarrow N_2 + O_2 \quad (15.8.2)$$

$$N_2O + O \rightarrow NO + NO \quad (15.8.3)$$

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Table 15.2 Major Stack Gas Scrubbing Systems[1]

Process	Reaction	Significant advantages or disadvantages
Lime slurry scrubbing[2]	$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O$	Up to 200 kg of lime are needed per metric ton of coal, producing huge quantities of wastes
Limestone slurry scrubbing[2]	$CaCO_3 + SO_2 \rightarrow CaSO_3 + CO_2(g)$	Lower pH than lime slurry, not so efficient
Magnesium oxide scrubbing	$Mg(OH)_2(slurry) + SO_2 \rightarrow MgSO_3 + H_2O$	The sorbent can be regenerated, which can be done off site, if desired.
Sodium-base scrubbing	$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$ $2NaHSO_3 + \text{heat} \rightarrow Na_2SO_3 + H_2O + SO_2$ (regeneration)	No major technological limitations. Relatively high annual costs.
Double alkali[2]	$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$ $Ca(OH)_2 + Na_2SO_3 \rightarrow CaSO_3(s) + 2NaOH$ (regeneration of NaOH)	Allows for regeneration of expensive sodium alkali solution with inexpensive lime.

[1] For details regarding these and more-advanced processes see (1) Satriana, M., *New Developments in Flue Gas Desulfurization Technology*, Noyes Data Corp., Park Ridge, NJ, 1982, and (2) Lunt, R., Arthur D. Little, and J.D. Cunic, *Profiles in Flue Gas Desulfurization*, American Institute of Chemical Engineers, New York, NY, 2000.

[2] These processes have also been adapted to produce a gypsum product by oxidation of $CaSO_3$ in the spent scrubber medium:

$$CaSO_3 + {}^1/_2O_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$$

Gypsum has some commercial value, such as in the manufacture of plasterboard, and makes a relatively settleable waste product.

These reactions are significant in terms of depletion of the ozone layer. Increased global fixation of nitrogen, accompanied by increased microbial production of N_2O, could contribute to ozone layer depletion.

Colorless, odorless nitric oxide (NO) and pungent red-brown nitrogen dioxide (NO_2) are very important in polluted air. Collectively designated NO_x, these gases enter the atmosphere from natural sources, such as lightning and biological processes, and from pollutant sources. The latter are much more significant because of regionally high NO_2 concentrations, which can cause severe air quality deterioration. Practically all anthropogenic NO_2 enters the atmosphere as a result of the combustion of fossil fuels in both stationary and mobile sources. The contribution of automobiles to nitric oxide production in the U.S. has become somewhat lower in the last decade as newer automobiles with nitrogen oxide pollution controls have become more common.

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Most NO_2 entering the atmosphere from pollution sources does so as NO generated from internal combustion engines. At the very high temperatures in an automobile combustion chamber, the following reaction occurs:

$$N_2 + O_2 \rightarrow 2NO \quad (15.8.4)$$

High temperatures favor both a high equilibrium concentration and a rapid rate of formation of NO. Rapid cooling of the exhaust gas from combustion "freezes" NO at a relatively high concentration because equilibrium is not maintained. Thus, by its very nature, the combustion process both in the internal combustion engine and in furnaces produces high levels of NO in the combustion products.

Atmospheric Reactions of NO_x

Atmospheric chemical reactions convert NO_x to nitric acid, inorganic nitrate salts, organic nitrates, and peroxyacetyl nitrate (see Chapter 16). The principal reactive nitrogen oxide species in the troposphere are NO, NO_2, and HNO_3. These species cycle among each other, as shown in Figure 15.9. Although NO is the primary form in which NO_x is released to the atmosphere, the conversion of NO to NO_2 is relatively rapid in the troposphere.

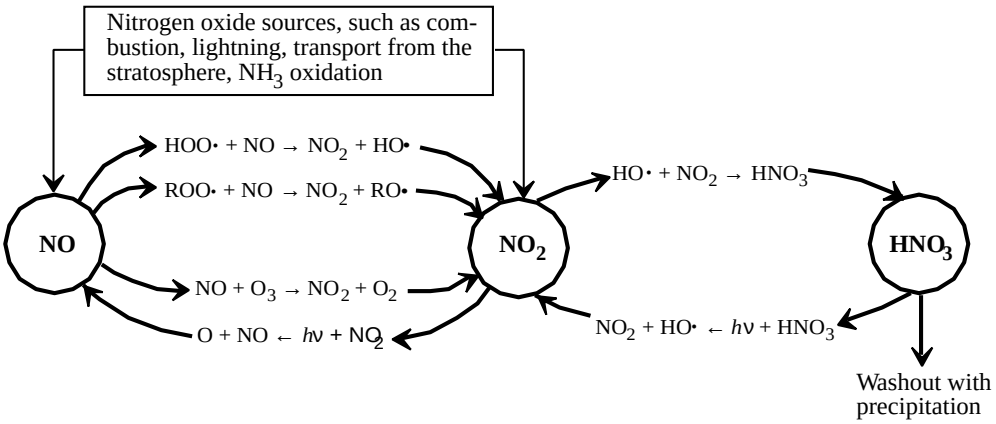


Figure 15.9 Principal reactions among NO, NO_2, and HNO_3 in the atmosphere. ROO• represents an organic peroxyl radical, such as the methylperoxyl radical, CH_3OO•.

Nitrogen dioxide is a very reactive and significant species in the atmosphere. It absorbs light throughout the ultraviolet and visible spectrum penetrating the troposphere. At wavelengths below 398 nm, photodissociation to oxygen atoms occurs,

$$NO_2 + h\nu \rightarrow NO + O \quad (15.8.5)$$

giving rise to several significant inorganic reactions, in addition to a host of atmospheric reactions involving organic species. The reactivity of NO_2 to photodissociation is shown clearly by the fact that in direct sunlight the half-life of NO_2 is much shorter than that of any other atmospheric component (only 1 or 2 minutes).

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Harmful Effects of Nitrogen Oxides

Nitric oxide, NO, is biochemically less active and less toxic than NO_2. Acute exposure to NO_2 can be quite harmful to human health. For exposures ranging from several minutes to 1 hour, a level of 50–100 ppm of NO_2 causes inflammation of lung tissue for a period of 6–8 weeks, after which time the subject normally recovers. Exposure of the subject to 150–200 ppm of NO_2 causes *bronchiolitis fibrosa obliterans*, a condition fatal within 3–5 weeks after exposure. Death generally results within 2–10 days after exposure to 500 ppm or more of NO_2. "Silo-filler's disease," caused by NO_2 generated by the fermentation of ensilage containing nitrate, is a particularly striking example of nitrogen dioxide poisoning. Deaths have resulted from the inhalation of NO_2-containing gases from burning celluloid and nitrocellulose film and from spillage of NO_2 oxidant from missile rocket motors.

Although extensive damage to plants is observed in areas receiving heavy exposure to NO_2, most of this damage probably comes from secondary products of nitrogen oxides, such as PAN formed in smog (see Chapter 16). Exposure of plants to several parts per million of NO_2 in the laboratory causes leaf spotting and breakdown of plant tissue. Exposure to 10 ppm of NO causes a reversible decrease in the rate of photosynthesis.

Nitrogen oxides are known to cause fading of dyes used in some textiles. This has been observed in gas clothes dryers and is due to NO_x formed in the dryer flame. Much of the damage to materials caused by NO_x, stress-corrosion cracking of electrical apparatus, comes from secondary nitrates and nitric acid.

Control of Nitrogen Oxides

The level of NO_x emitted from stationary sources such as power plant furnaces generally falls within the range of 50–1000 ppm. NO production is favored both kinetically and thermodynamically by high temperatures and by high excess oxygen concentrations. These factors must be considered in reducing NO emissions from stationary sources. Reduction of flame temperature to prevent NO formation is accomplished by adding recirculated exhaust gas, cool air, or inert gases.

Low-excess-air firing is effective in reducing NO_x emissions during the combustion of fossil fuels. As the term implies, low-excess-air firing uses the minimum amount of excess air required for oxidation of the fuel, so that less oxygen is available for the reaction

$$N_2 + O_2 \rightarrow 2NO_2 \tag{15.8.6}$$

in the high temperature region of the flame. Incomplete fuel burnout, with the emission of hydrocarbons, soot, and CO, is an obvious problem with low-excess-air firing. This may be overcome by a two-stage combustion process. In the first stage, fuel is fired at a relatively high temperature with a substoichiometric amount of air, and NO formation is limited by the absence of excess oxygen. In the second stage, fuel burnout is completed at a relatively low temperature in excess air; the low temperature prevents formation of NO.

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Removal of NO_x from stack gas presents some formidable problems. Possible approaches to NO_x removal are catalytic decomposition of nitrogen oxides, catalytic reduction of nitrogen oxides, and sorption of NO_x by liquids or solids.

Ammonia in the Atmosphere

Ammonia is present even in unpolluted air as a result of natural biochemical and chemical processes. Among the various sources of atmospheric ammonia are microorganisms, decay of animal wastes, sewage treatment, coke manufacture, ammonia manufacture, and leakage from ammonia-based refrigeration systems. High concentrations of ammonia gas in the atmosphere are generally indicative of accidental release of the gas.

Ammonia is removed from the atmosphere by its affinity for water and by its action as a base. It is a key species in the formation and neutralization of nitrate and sulfate aerosols in polluted atmospheres. Ammonia reacts with these acidic aerosols to form ammonium salts:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \quad (15.8.7)$$

$$NH_3 + H_2SO_4 \rightarrow NH_4HSO_3 \quad (15.8.8)$$

Ammonium salts are among the more corrosive salts in atmospheric aerosols.

15.9. ACID RAIN

As discussed in this chapter, much of the sulfur and nitrogen oxides entering the atmosphere are converted to sulfuric and nitric acids, respectively. These, combined with hydrochloric acid arising from hydrogen chloride emissions, cause acidic precipitation that is now a major pollution problem in some areas.

Precipitation made acidic by the presence of acids stronger than $CO_2(aq)$ is commonly called **acid rain**; the term applies to all kinds of acidic aqueous precipitation, including fog, dew, snow, and sleet. In a more general sense, **acid deposition** refers to the deposition on the earth's surface of aqueous acids, acid gases (such as SO_2), and acidic salts (such as NH_4HSO_4). According to this definition, deposition in solution form is *acid precipitation*, and deposition of dry gases and compounds is *dry deposition*. Although carbon dioxide is present at higher levels in the atmosphere, sulfur dioxide, SO_2, contributes more to the acidity of precipitation for two reasons. The first of these is that sulfur dioxide is significantly more soluble in water than is carbon dioxide, as indicated by its Henry's law constant (Section 5.3) of 1.2 mol × L^{-1} × atm^{-1} compared to 3.38×10^{-2} mol × L^{-1} × atm^{-1} for CO_2. Secondly, the value of K_{a1} for $SO_2(aq)$,

$$SO_2(aq) + H_2O \leftarrow \rightarrow H^+ + HSO_3^- \quad (15.9.1)$$

$$K_{a1} = \frac{[H^+][HSO_3^-]}{[SO_2]} = 1.7 \times 10^{-2} \quad (15.9.2)$$

is more than four orders of magnitude higher than the value of 4.45×10^{-7} for CO_2.

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Although acid rain can originate from the direct emission of strong acids, such as HCl gas or sulfuric acid mist, most of it is a secondary air pollutant produced by the atmospheric oxidation of acid-forming gases such as the following:

$$SO_2 + {}^1/_2O_2 + H_2O \xrightarrow{\text{Overall reaction consisting of several steps}} \{2H^+ + SO_4^{2-}\}(aq) \qquad (15.9.3)$$

$$2NO_2 + {}^1/_2O_2 + H_2O \xrightarrow{\text{Overall reaction consisting of several steps}} 2\{H^+ + NO_3^-\}(aq) \qquad (15.9.4)$$

Chemical reactions such as these play a dominant role in determining the nature, transport, and fate of acid precipitation. As the result of such reactions, the chemical properties (acidity, ability to react with other substances) and physical properties (volatility, solubility) of acidic atmospheric pollutants are altered drastically. For example, even the small fraction of NO that does dissolve in water does not react significantly. However, its ultimate oxidation product, HNO_3, though volatile, is highly water-soluble, strongly acidic, and very reactive with other materials. Therefore, it tends to be removed readily from the atmosphere and to do a great deal of harm to plants, corrodible materials, and other things that it contacts.

Although emissions from industrial operations and fossil fuel combustion are the major sources of acid-forming gases, acid rain has also been encountered in areas far from such sources. This is due in part to the fact that acid-forming gases are oxidized to acidic constituents and deposited over several days, during which time the air mass containing the gas may have moved as much as several thousand km. It is likely that the burning of biomass, such as is employed in “slash-and-burn” agriculture evolves the gases that lead to acid formation in more-remote areas. In arid regions, dry acid gases or acids sorbed to particles may be deposited with effects similar to those of acid rain deposition.

Acid rain spreads out over areas of several hundred to several thousand kilometers. This classifies it as a *regional* air pollution problem rather than a *local* air pollution problem for smog and a *global* one for ozone-destroying chlorofluorocarbons and greenhouse gases. Other examples of regional air pollution problems are those caused by soot, smoke, and fly ash from combustion sources and fires (forest fires). Nuclear fallout from weapons testing or from reactor fires (of which, fortunately, there has been only one major one to date—the one at Chernobyl in the former Soviet Union) can also be regarded as a regional phenomenon.

Acid precipitation shows a strong geographic dependence, as illustrated in Figure 15.10, representing the pH of precipitation in the continental U.S. The preponderance of acidic rainfall in the northeastern U.S., which also affects southeastern Canada, is obvious. Analyses of the movements of air masses have shown a correlation between acid precipitation and prior movement of an air mass over major sources of anthropogenic sulfur and nitrogen oxides emissions. This is particularly obvious in southern Scandinavia, which receives a heavy burden of air pollution from densely populated, heavily industrialized areas in Europe.

Acid rain has been observed for well over a century, with many of the older observations from Great Britain. The first manifestations of this phenomenon were elevated levels of SO_4^{2-} in precipitation collected in industrialized areas. More modern evidence was obtained from analyses of precipitation in Sweden in the 1950s, and of U.S. precipitation a decade or so later. A vast research effort on acid rain was

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conducted in North America by the National Acid Precipitation Assessment Program, which resulted from the U.S. Acid Precipitation Act of 1980.

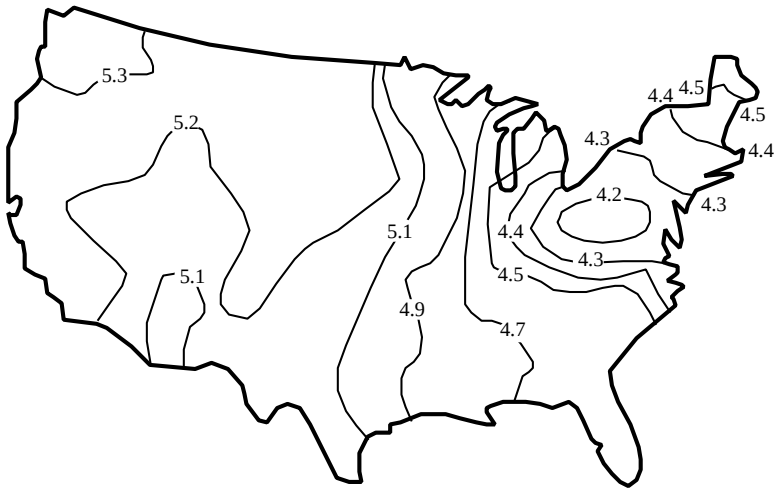


Figure 15.10 Isopleths of pH illustrating a hypothetical precipitation-pH pattern in the lower 48 continental United States. Actual values found may vary with the time of year and climatic conditions.

The longest-term experimental study of acid precipitation in the U.S. has been conducted at the U.S. Forest Service Hubbard Brook Experimental Forest in New Hampshire's White Mountains. It is downwind from major U.S. urban and industrial centers and is, therefore, a prime candidate to receive acid precipitation. This is reflected by mean annual pH values ranging from 4.0 to 4.2 during the 1964–74 period. During this period, the annual hydrogen ion input ($[H^+]$ × volume) increased by 36%.

Table 15.3 shows typical major cations and anions in pH-4.25 precipitation. Although actual values encountered vary greatly with time and location of collection, this table does show some major features of ionic solutes in precipitation. The predominance of sulfate anion shows that sulfuric acid is the major contributor to acid precipitation. Nitric acid makes a smaller, but significant, contribution to the acid present. Hydrochloric acid ranks third.

It is useful to distinguish between primary sulfate species emitted directly by point sources and secondary sulfate species formed from gaseous sulfur compounds, primarily by the atmospheric oxidation of SO_2. A low primary-sulfate content indicates transport of the pollutant from some distance, whereas a high primary-sulfate content indicates local emissions (the high water solubility of sulfate species means that they do not move far from their sources before being removed with precipitation). This information can be useful in determining the effectiveness of SO_2 control in reducing atmospheric sulfate, including sulfuric acid. Primary and secondary sulfates can be measured using the oxygen-18 content of the sulfates, which is higher in sulfate emitted directly from a power plant than it is in sulfate formed by the oxidation of SO_2.

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Table 15.3 Typical Values of Ion Concentrations in Acidic Precipitation

Cations		Anions	
Ion	Concentration equivalents/L $\times 10^6$	Ion	Concentration equivalents/L $\times 10^6$
H^+	56	SO_4^{2-}	51
NH_4^+	10	NO_3^-	20
Ca^{2+}	7	Cl^-	12
Na^+	5	Total	83
Mg^{2+}	3		
K^+	2		
Total	83		

Ample evidence exists of the damaging effects of acid rain. The major effects are the following:

- Direct phytotoxicity to plants from excessive acid concentrations. (Evidence of direct or indirect phytoxicity of acid rain is provided by the declining health of eastern U.S. and Scandinavian forests and especially by damage to Germany's Black Forest.)
- Phytotoxicity from acid-forming gases, particularly SO_2 and NO_2, that accompany acid rain
- Indirect phytotoxicity, such as from Al^{3+} liberated from soil
- Destruction of sensitive forests
- Respiratory effects on humans and other animals
- Acidification of lake water with toxic effects to lake flora and fauna, especially fish fingerlings
- Corrosion of exposed structures, electrical relays, equipment, and ornamental materials. Because of the effect of hydrogen ion,

 $$2H^+ + CaCO_3(s) \rightarrow Ca^{2+} + CO_2(g) + H_2O$$

 limestone, $CaCO_3$, is especially susceptible to damage from acid rain
- Associated effects, such as reduction of visibility by sulfate aerosols and the influence of sulfate aerosols on physical and optical properties of clouds. (As mentioned in Section 15.6, intensification of cloud cover and changes in the optical properties of cloud droplets—specifically, increased reflectance of light—resulting from acid sulfate in the atmosphere may even have a mitigating effect on greenhouse warming of the atmosphere.) A significant association exists between acidic sulfate in the atmosphere and haziness.

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Forms of precipitation other than rainfall may contain excess acidity. Acidic fog can be especially damaging because it is very penetrating. In early December 1982, Los Angeles experienced a severe, 2-day episode of acid fog. This fog consisted of a heavy concentration of acidic mist particles at ground level that reduced visibility and were very irritating to breathe. The pH of the water in these particles was 1.7, much lower than ever before recorded for acid precipitation. Another source of precipitation heavy in the ammonium, sulfate, and nitrate ions associated with atmospheric acid is **acid rime**. Rime is frozen cloudwater that may condense on snowflakes or exposed surfaces. Rime constitutes up to 60% of the snowpack in some mountainous areas, and the deposition of acidic constituents with rime may be a significant vector for the transfer of acidic atmospheric constituents to Earth's surface in some cases.

15.10 FLUORINE, CHLORINE, AND THEIR GASEOUS COMPOUNDS

Fluorine, hydrogen fluoride, and other volatile fluorides are produced in the manufacture of aluminum, and hydrogen fluoride is a byproduct in the conversion of fluorapatite (rock phosphate) to phosphoric acid, superphosphate fertilizers, and other phosphorus products. Hydrogen fluoride gas is a dangerous substance that is so corrosive that it even reacts with glass. It is irritating to body tissues, and the respiratory tract is very sensitive to it. Brief exposure to HF vapors at the part-per-thousand level may be fatal. The acute toxicity of F_2 is even higher than that of HF. Chronic exposure to high levels of fluorides causes fluorosis. The symptoms of fluorosis include mottled teeth and pathological bone conditions that can be manifested by defective bone structure.

Plants are particularly susceptible to the effects of gaseous fluorides. Fluorides from the atmosphere appear to enter the leaf tissue through the stomata. Fluoride is a cumulative poison in plants, and exposure of sensitive plants to even very low levels of fluorides for prolonged periods results in damage. Characteristic symptoms of fluoride poisoning are chlorosis (fading of green color due to conditions other than the absence of light), edge burn, and tip burn. Conifers (such as pine trees) afflicted with fluoride poisoning may have reddish-brown necrotic needle tips.

Silicon tetrafluoride gas, SiF_4, a gaseous fluoride pollutant produced during some steel and metal smelting operations that employ CaF_2, fluorspar. Fluorspar reacts with silicon dioxide (sand), releasing SiF_4 gas:

$$2CaF_2 + 3SiO_2 \rightarrow 2CaSiO_3 + SiF_4 \qquad (15.10.1)$$

Another gaseous fluorine compound, sulfur hexafluoride, SF_6, occurs in the atmosphere at levels of about 0.3 parts per trillion. It is extremely unreactive with an atmospheric lifetime estimated at 3200 years, and is used as an atmospheric tracer. It does not absorb ultraviolet light in either the troposphere or stratosphere, and is probably destroyed above 60 km by reactions beginning with its capture of free electrons. Current atmospheric levels of SF_6 are significantly higher than the estimated background level of 0.04 ppt in 1953, when commercial production of it began. The compound is very useful in specialized applications including gas-insulated electrical equipment and inert blanketing/degassing of molten aluminum and

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magnesium. Increasing uses of sulfur hexafluoride are of concern because it is the most powerful greenhouse gas known, with a global warming potential (per molecule added to the atmosphere) about 23,900 times that of carbon dioxide.

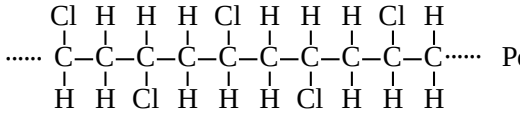
Chlorine and Hydrogen Chloride

Chlorine gas, Cl_2, does not occur as an air pollutant on a large scale but can be quite damaging on a local scale. Chlorine was the first poisonous gas deployed in World War I. It is widely used as a manufacturing chemical, in the plastics industry, for example, as well as for water treatment and as a bleach. Therefore, possibilities for its release exist in a number of locations. Chlorine is quite toxic and is a mucous-membrane irritant. It is very reactive and a powerful oxidizing agent. Chlorine dissolves in atmospheric water droplets, yielding hydrochloric acid and hypochlorous acid, an oxidizing agent:

$$H_2O + Cl_2 \rightarrow H^+ + Cl^- + HOCl \qquad (15.10.2)$$

Spills of chlorine gas have caused fatalities among exposed persons.

Hydrogen chloride, HCl, is emitted from a number of sources. Incineration of chlorinated plastics, such as polyvinylchloride, releases HCl from combustion.



Polyvinylchloride

Some compounds released to the atmosphere as air pollutants hydrolyze to form HCl. Such incidents have occurred as the result of leaks of liquid silicon tetrachloride, $SiCl_4$. This compound reacts with water in the atmosphere to form a choking fog of hydrochloric acid droplets:

$$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl \qquad (15.10.3)$$

Other incidents have occurred when powdered aluminum chloride has been spilled. This compound also produces HCl gas when wet,

$$AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3HCl \qquad (15.10.4)$$

generating fumes of hydrochloric acid.

15.11 HYDROGEN SULFIDE, CARBONYL SULFIDE, AND CARBON DISULFIDE

Hydrogen sulfide is produced by microbial decay of sulfur compounds and microbial reduction of sulfate (see the discussion of microbial transformation of sulfur in Chapter 11, Section 11.13), from geothermal steam, from wood pulping, and from a number of miscellaneous natural and anthropogenic sources. Most atmospheric hydrogen sulfide is rapidly converted to SO_2 and to sulfates. The organic homologs of hydrogen sulfide, the mercaptans, enter the atmosphere from decaying organic matter

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and have particularly objectionable odors.

Hydrogen sulfide pollution from artificial sources is not as much of an overall air pollution problem as sulfur dioxide pollution. However, there have been several acute incidents of hydrogen sulfide emissions resulting in damage to human health and even fatalities. The most notorious such incident occurred in Poza Rica, Mexico, in 1950. Accidental release of hydrogen sulfide from a plant used for the recovery of sulfur from natural gas caused the reported deaths of 22 people and the hospitalization of over 300.

Hydrogen sulfide at levels well above ambient concentrations destroys immature plant tissue. This type of plant injury is readily distinguished from that due to other phytotoxins. More-sensitive species are killed by continuous exposure to around 3000 ppb H_2S, whereas other species exhibit reduced growth, leaf lesions, and defoliation.

Damage to certain kinds of materials is a very expensive effect of hydrogen sulfide pollution. Paints containing lead pigments, $2PbCO_3 \cdot Pb(OH)_2$ (no longer used), were particularly susceptible to darkening by H_2S. A black layer of copper sulfide forms on copper metal exposed to H_2S. Eventually, this layer is replaced by a green coating of basic copper sulfate such as $CuSO_4 \cdot 3Cu(OH)_2$. The green "patina," as it is called,is very resistant to further corrosion. Such layers of corrosion can seriously impair the function of copper contacts on electrical equipment. Hydrogen sulfide also forms a black sulfide coating on silver.

Carbonyl sulfide, COS, is now recognized as a component of the atmosphere at a tropospheric concentration of approximately 500 parts per trillion by volume, corresponding to a global burden of about 2.4 teragrams. It is, therefore, a significant sulfur species in the atmosphere.

Both COS and CS_2 are oxidized in the atmosphere by reactions initiated by the hydroxyl radical. The initial reactions are

$$HO\bullet + COS \rightarrow CO_2 + HS\bullet \quad (15.11.1)$$

$$HO\bullet + CS_2 \rightarrow COS + HS\bullet \quad (15.11.2)$$

The sulfur-containing products undergo further reactions to sulfur dioxide and, eventually, to sulfate species.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Atmospheric aerosols are [1]_____ _____. Condensation aerosols are formed by [2]_____ and dispersion aerosols are formed by [3]_____ _____. As applied to the formation of atmospheric aerosols, the reaction $2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$ shows[4]_____ _____

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_____. In general, the proportions of elements in atmospheric particulate matter reflect[5]_____ _____. The two reactions $2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$ and $H_2SO_4 + 2NaCl(particulate) \rightarrow 2Na_2SO_4(particulate) + 2HCl$ show why particulate matter largely from ocean spray origin in a coastal area receiving sulfur dioxide pollution may show [6]_____ _____. Insofar as origins of elements in particulate matter are concerned, soil erosion, rock dust, and coal combustion produce [7]_____ _____; incomplete combustion of carbonaceous fuels produces [8]_____; marine aerosols and incineration of organohalide polymer wastes produces [9]_____ _____; and combustion of residual petroleum produces [10]_____. Mineral particulate matter in the form of oxides and other compounds produced during the combustion of high-ash fossil fuel that can be collected in furnace flues is called [11]_____. Three adverse respiratory health effects caused by inhalation of asbestos are [12]_____ _____. The toxic metal of greatest concern in the urban atmosphere is [13]_____ because it [14]_____ _____. A significant natural source of radionuclides in the atmosphere is [15]_____,which initially decays to [16]_____. Another significant source of radioactivity in the atmosphere is [17]_____ _____ and a former source of atmospheric radioactivity was [18] _____. Three effects of atmospheric particles are [19] _____. The most common health effects of atmospheric particles are on the [20]_____ _____. Some of the most common ways to control particulate emissions are [21]_____ _____. Carbon monoxide causes pollution problems in cases of [22]_____. _____. It is of most concern because of its [23]_____. Automobiles are equipped with [24]_____ to cut down carbon monoxide emissions. It is generally agreed that carbon monoxide is removed from the atmosphere by [25]_____. The greatest pollution concern with carbon dioxide is its role as [26]_____ _____. The two major sources of atmospheric carbon dioxide are [27]_____. Most sulfates enter the atmosphere from [28]_____ and most sulfur dioxide from [29]_____. The fate of any H_2S that does get into the atmosphere is that it is [30]_____. Sulfur dioxide's primary health effect is upon the [31]_____. Chronic exposure of plants to sulfur dioxide causes [32]_____. Sulfur dioxide can be removed from stack gas by [33]_____ processes, of which the major types are [34]_____ _____. The three oxides of nitrogen normally encountered in the atmosphere are [35]_____. Nitric oxide (NO) and nitrogen dioxide (NO_2) are collectively designated [36]_____, most of which enters the atmosphere as [37]_____. The most important photo-chemical reaction of NO_2, and one that can lead to photochemical smog formation is [38]

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. Pulmonary exposure to 150–200 ppm of NO_2 causes [39] , a condition fatal within 3–5 weeks after exposure. During the combustion of fossil fuels, [40]_____ _____ is effective in reducing NO_x emissions. Sources of atmospheric ammonia are [41]_____ _____ _____Much of the sulfur and nitrogen oxides entering the atmosphere are converted to [42]_____ _____, which, along with hydrochloric acid arising from hydrogen chloride emissions, cause [43]_____. The major damaging effects of acid precipitation are [44]_____ _____ _____ _____ _____ _____ _____ _____. Two specific gaseous fluorine-containing air pollutants are [45]_____ _____. Though not directly toxic, the fluorine-containing air pollutants with the greatest potential for damage to the atmosphere are the [46]_____ _____. Halons, which are related to chlorofluorocarbons, are compounds that contain [47]_____ and are used in [48] . The concern with chlorofluoro-carbon air pollutants is [49] . The first reaction in this harmful process is [50]_____, the Cl atoms of which undergo the reaction [51] with ozone. The most prominent instance of ozone layer destruction that has been documented in recent years is [52]_____. The highly damaging conse-quence of stratospheric ozone destruction is that it would allow [53] _____, which would result in [54]_____ _____. Atmospheric chlorine dissolves in atmospheric water droplets, yielding [55]_____. Natural sources of hydrogen sulfide are [56]_____ _____.

Answers to Chapter Summary

1. solid or liquid particles smaller than 100 μm in diameter
2. condensation of vapors or reactions of gases
3. grinding of solids, atomization of liquids, aerosol or dispersion of dusts
4. oxidation of atmospheric sulfur dioxide to sulfuric acid, a hygroscopic sub-stance that accumulates atmospheric water to form small liquid droplets
5. relative abundances of elements in the parent material
6. anomalously high sulfate and corresponding low chloride content
7. Al, Fe, Ca, Si
8. C
9. Na, Cl
10. V

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11. fly ash
12. asbestosis, mesothelioma, and bronchogenic carcinoma
13. lead
14. comes closest to being present at a toxic level
15. radon
16. ^{218}Po and ^{216}Po
17. the combustion of fossil fuels
18. the above-ground detonation of nuclear weapons
19. reduction and distortion of visibility, provision of active surfaces upon which heterogeneous atmospheric chemical reactions can occur, and nucleation bodies for the condensation of atmospheric water vapor
20. respiratory tract
21. sedimentation, inertial mechanisms, baghouses, scrubbers, electrostatic precipitators
22. concentrated localized pollution
23. toxicity
24. catalytic converters
25. reaction with hydroxyl radical
26. a greenhouse gas
27. burning of fossil fuels and deforestation
28. marine sources
29. scrubbing
30. converted rapidly to SO_2
31. respiratory tract
32. chlorosis
33. scrubbing
34. throwaway and recovery systems
35. nitrous oxide (N_2O), nitric oxide (NO), and nitrogen dioxide (NO_2)
36. NO_x
37. NO
38. $NO_2 + h\nu \rightarrow NO + O$
39. *bronchiolitis fibrosa obliterans*
40. low excess air firing
41. microorganisms, decay of animal wastes, sewage treatment, coke manufacture, ammonia manufacture, and leakage from ammonia-based refrigeration systems
42. sulfuric and nitric acids
43. acidic precipitation
44. direct phytotoxicity to plants from excessive acid concentrations; phytotoxicity from acid-forming gases; indirect phytotoxicity, such as from Al^{3+} liberated from acidified soil; destruction of sensitive forests, respiratory effects on humans and other animals; acidification of lake water with toxic effects to lake flora and fauna; corrosion to exposed structures, electrical relays, equipment, and ornamental materials; and associated effects, such as reduction of visibility by sulfate aerosols and the influence of sulfate aerosols on physical and optical properties of clouds.
45. fluorine gas and hydrogen fluoride
46. chlorofluorocarbons (CFC)
47. bromine

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48. fire extinguisher systems
49. their potential to destroy stratospheric ozone
50. $Cl_2CF_2 + h\nu \rightarrow Cl\cdot + ClCF_2\cdot$
51. $Cl + O_3 \rightarrow ClO + O_2$
52. the Antarctic ozone hole
53. penetration of high-energy ultraviolet radiation
54. adverse biological effects, such as increased skin cancer
55. hydrochloric acid and hypochlorous acid
56. microbial decay of sulfur compounds and microbial reduction of sulfate

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QUESTIONS AND PROBLEMS

1. A freight train that included a tank car containing anhydrous NH_3 and one containing concentrated HCl was wrecked, causing both of the tank cars to leak. In the region between the cars a white aerosol formed. What was it, and how was it produced?
2. What two vapor forms of mercury might be found in the atmosphere?
3. Analysis of particulate matter collected in the atmosphere near a seashore shows considerably more Na than Cl on a molar basis. What does this indicate?
4. What type of process results in the formation of very small aerosol particles?
5. Which size range encompasses most of the particulate matter mass in the atmosphere?
6. Why are aerosols in the 0.1–1 μm size range especially effective in scattering light?
7. Per unit mass, why are smaller particles more effective catalysts for atmospheric chemical reactions?
8. What is the rationale for classifying most acid rain as a secondary pollutant?
9. Distinguish among UV-A, UV-B, and UV-C radiation. Why does UV-B pose the greatest danger in the troposphere?
10. Why is it that "highest levels of carbon monoxide tend to occur in congested urban areas at times when the maximum number of people are exposed?"
11. Which unstable, reactive species is responsible for the removal of CO from the atmosphere?
12. Which of the following fluxes in the atmospheric sulfur cycle is smallest: (a) Sulfur species washed out in rainfall over land, (b) sulfates entering the atmosphere as "sea salt," (c) sulfur species entering the atmosphere from volcanoes, (d) sulfur species entering the atmosphere from fossil fuels, (e) hydrogen sulfide entering the atmosphere from biological processes in coastal areas and on land.
13. Of the following agents, the one that would not favor conversion of sulfur dioxide to sulfate species in the atmosphere is: (a) Ammonia, (b) water, (c) contaminant reducing agents, (d) ions of transition metals such as manganese, (e) sunlight.
14. The air inside a garage was found to contain 10 ppm CO by volume at standard temperature and pressure (STP). What is the concentration of CO in mg/L and in ppm by mass?
15. Assume that an incorrectly adjusted lawn mower is operated in a garage such that the combustion reaction in the engine is

$$C_8H_{18} + {}^{17}/_2O_2 \rightarrow 8CO + 9H_2O$$

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If the dimensions of the garage are 5 × 3 × 3 meters, how many grams of gasoline must be burned to raise the level of CO in the air to 1000 ppm by volume at STP?

16. A 12.0-L sample of waste air from a smelter process was collected at 25˚C and 1.00 atm pressure, and the sulfur dioxide was removed. After SO_2 removal, the volume of the air sample was 11.50 L. What was the percentage by weight of SO_2 in the original sample?

17. What is the oxidant in the Claus reaction?

18. How many metric tons of 5%–S coal would be needed to yield the H_2SO_4 required to produce a 3.00–cm rainfall of pH 2.00 over a 100 km^2 area?

19. In what major respect is NO_2 a more significant species than SO_2 in terms of participation in atmospheric chemical reactions?

20. Match the effect on the right with its most likely source or cause from the left, below:

A. Sunlight and autos	1. Global warming
B. Burning of all types of fossil fuels	2. Increased acidity in the atmosphere
C. Chlorofluorocarbons	3. Pollutant oxidants in the lower troposphere
D. Burning of coal, especially	4. Destruction of stratospheric ozone

21. Of the following, the most likely to be formed by pyrosynthesis is

 A. Sulfate particles
 B. Ammonium particles
 C. Sulfuric acid mist
 D. PAHs
 E. Ozone in smog

22. Of the following, the true statement related to carbon monoxide in the atmosphere is

 A. It is strictly a pollutant with none coming from natural sources.
 B. It is an intermediate in reactions by which methane is removed by normal atmospheric processes.
 C. It is increasing in the atmosphere at a rate of approximately 1 ppm per year.
 D. Although produced by a reaction with hydroxyl radical it does not react with HO•.
 E. Most harmful levels of CO are produced as secondary pollutants.

23. Of the following, the **untrue** statement regarding the fate of sulfur dioxide in the atmosphere is

 A. It reacts to form particulate matter.
 B. It is largely oxidized by reactions occurring inside water aerosol droplets.
 C. Although acidic, it can react to form an even more acidic species.
 D. The presence of hydrocarbons and nitrogen oxides generally accelerates sulfur dioxide oxidation.
 E. It is produced as a stable species during smog-forming conditions.

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24. Assume that the wet limestone process requires 1 metric ton of $CaCO_3$ to remove 90% of the sulfur from 4 metric tons of coal containing 2% S. Assume that the sulfur product is $CaSO_4$. Calculate the percentage of the limestone converted to calcium sulfate.

25. Of the following, the statement that is **untrue** is

 A. Acid rain is denoted by any precipitation with a pH less than neutral (7.00).
 B. Acid may be deposited as acidic salts and acid gases, in addition to liquid acid rain
 C. Acid rain is a regional air pollution problem as distinguished from local or global problems.
 D. Carbon dioxide makes rainfall slightly acidic
 E. Acid rain is often associated with elevated levels of sulfate ion, SO_4^{2-}.

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Manahan, Stanley E. "ORGANIC AIR POLLUTANTS AND PHOTOCHEMICAL SMOG"
Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC,2001

16 ORGANIC AIR POLLUTANTS AND PHOTOCHEMICAL SMOG

16.1 ORGANIC COMPOUNDS IN THE ATMOSPHERE

Organic pollutants may have a strong effect upon atmospheric quality. The effects of organic pollutants in the atmosphere can be divided into two major categories. The first consists of **direct effects**, such as cancer caused by exposure to vinyl chloride. The second is the formation of **secondary pollutants**, especially photochemical smog, discussed later in this chapter. In the case of pollutant hydrocarbons in the atmosphere, the latter is the more important effect. In some localized situations, particularly the workplace, direct effects of organic air pollutants may be equally important.

Global Distillation and Fractionation of Persistent Organic Pollutants

On a global scale, it is likely that persistent organic pollutants undergo a cycle of distillation and fractionation in which they are vaporized into the atmosphere in warmer regions of the Earth and condense and are deposited in colder regions. The theory of this phenomenon holds that the distribution of such pollutants is governed by their physicochemical properties and the temperature conditions to which they are exposed. As a result, the least volatile persistent organic pollutants are deposited near their sources, those of relatively high volatility are distilled into polar regions, and those of intermediate volatility are deposited predominantly at mid latitudes. This phenomeonon has some important implications regarding the accumulation of persistent organic pollutants in environmentally fragile polar regions and cold mountainous areas far from industrial sources.

Reactions and Fates of Organic Compounds

Much of the remainder of this chapter deals with the reactions and fates of organic compounds in the atmosphere, especially in respect to how these processes lead to the formation of the common air pollution problem of photochemical smog.

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There are two important points related to what happens to organic compounds in the atmosphere. The first of these is the importance of photochemical reactions initiated by the absorption of photons of electromagnetic radiation, usually of wavelengths in the ultraviolet region just a bit shorter than those of visible light. The energy of these photons is equal to the product of Planck's constant, *h*, and the frequency of the radiation, ν. Therefore, the product $h\nu$ is used to represent photons of electromagnetic radiation in photochemical reactions. The second crucial point regarding the fates of organic species in the atmosphere is the central role played by the highly reactive hydroxyl radical represented HO•. This is a free radical species meaning that it has an unpaired electron, which is what the dot in the formula represents. Hydroxyl radical is involved in virtually all the pathways by which organic compounds react in the atmosphere and by which photochemical smog is formed.

16.2 ORGANIC COMPOUNDS FROM NATURAL SOURCES

Natural sources are the most important contributors of organics in the atmosphere, and hydrocarbons generated and released by human activities consitute only about 1/7 of the total hydrocarbons in the atmosphere. This ratio is primarily the result of the huge quantities of methane produced by anaerobic bacteria in the decomposition of organic matter in water, sediments, and soil:

$$2\{CH_2O\}\ \text{(bacterial action)} \rightarrow CO_2(g) + CH_4(g) \qquad (16.2.1)$$

Flatulent emissions from domesticated animals, arising from bacterial decomposition of food in their digestive tracts, add about 85 million metric tons of methane to the atmosphere each year. Anaerobic conditions in intensively cultivated rice fields produce large amounts of methane, perhaps as much as 100 million metric tons per year. Methane is a natural constituent of the atmosphere and is present at a level of about 1.4 parts per million (ppm) in the troposphere.

Methane in the troposphere contributes to the photochemical production of carbon monoxide and ozone. The photochemical oxidation of methane is a major source of water vapor in the stratosphere.

Atmospheric hydrocarbons produced by living sources are called **biogenic hydrocarbons**. Vegetation is the most important natural source of non-methane biogenic compounds. Several hundred different hydrocarbons are released to the atmosphere from vegetation sources. Other natural sources include microorganisms, forest fires, animal wastes, and volcanoes.

One of the simplest organic compounds given off by plants is ethylene, C_2H_4. This compound is produced by a variety of plants and released to the atmosphere in its role as a messenger species regulating plant growth. Because of its double bond, ethylene is highly reactive with hydroxyl radical, HO•, and with oxidizing species in the atmosphere. Ethylene from vegetation sources should be considered as an active participant in atmospheric chemical processes.

Most of the hydrocarbons emitted by plants are **terpenes**, which constitute a large class of organic compounds found in essential oils. Essential oils are obtained when parts of some types of plants are subjected to steam distillation. Most of the plants that produce terpenes are conifers (evergreen trees and shrubs such as pine

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and cypress), plants of the genus *Myrtus*, and trees and shrubs of the genus *Citrus*. One of the most common terpenes emitted by trees is α-pinene, a principal component of turpentine. The terpene limonene, found in citrus fruit and pine needles, is encountered in the atmosphere around these sources. Isoprene (2-methyl-1,3-butadiene), a hemiterpene, has been identified in the emissions from cottonwood, eucalyptus, oak, sweetgum, and white spruce trees. Linalool is a terpene with the chemical formula $(CH_3)_2C{=}CHCH_2CH_2C(CH_3)(OH)CH{=}CH_2$, which is given off by some plant species common to Italy and Austria, including the pine *Pinus pinea* and orange blossoms. Other terpenes that are known to be given off by trees include β-pinene, myrcene, ocimene, and α-terpinene.

As exemplified by the structural formulas of α-pinene, β-pinene, Δ^3-carene, isoprene, and limonene, shown in Figure 16.1, terpenes contain alkenyl (olefinic) bonds, in some cases two or more per molecule. Because of these and other structural features, terpenes are among the most reactive compounds in the atmosphere. The reaction of terpenes with hydroxyl radical is very rapid, and terpenes also react with other oxidizing agents in the atmosphere, particularly ozone, O_3. Turpentine, a mixture of terpenes, has been widely used in paint because it reacts with atmospheric oxygen to form a peroxide, then a hard resin. It is likely that compounds such as α-pinene and isoprene undergo similar reactions in the atmos-

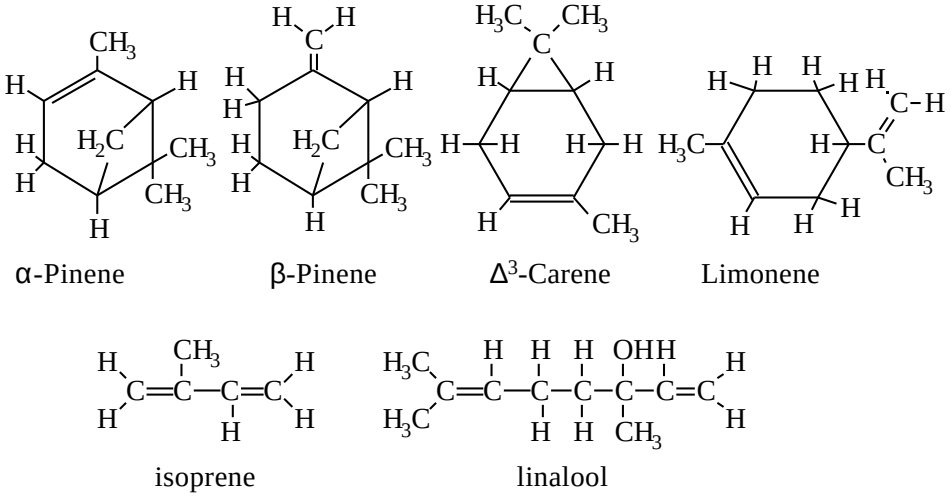
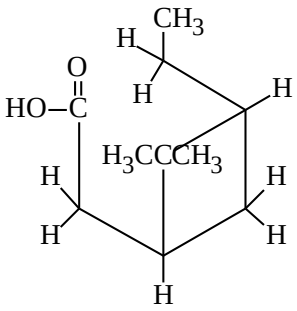


Figure 16.1 Some common terpenes emitted to the atmosphere by vegetation, primarily trees such as pine and citrus trees. These reactive compounds are involved in the formation of much of the small particulate matter encountered in the atmosphere.

phere to form particulate matter. These aerosols are a cause of the blue haze in the atmosphere above some heavy growths of vegetation.

Laboratory and smog-chamber experiments have been performed in an effort to determine the fates of atmospheric terpenes. When a mixture of α-pinene with NO and NO_2 in air is irradiated with ultraviolet light, pinonic acid is formed:

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Found in forest aerosol particles, this compound is produced by photochemical processes acting upon α-pinene.

Perhaps the greatest variety of compounds emitted by plants consists of **esters**. However, they are released in such small quantities that they have little influence upon atmospheric chemistry. Esters are primarily responsible for the fragrances associated with much vegetation. Some typical esters that are released by plants to the atmosphere are shown in Figure 16.2.

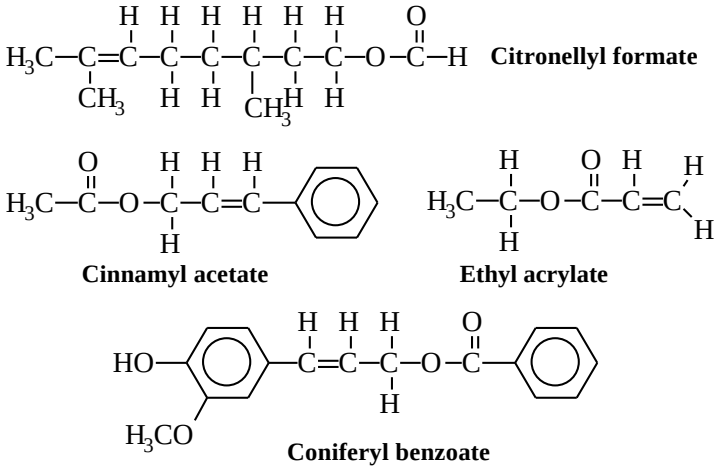
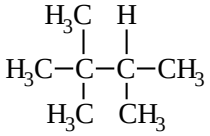


Figure 16.2 Examples of esters from natural sources that are found in the atmosphere.

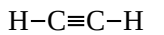
16.3 POLLUTANT HYDROCARBONS

Ethylene and terpenes, which were discussed in the preceding section, are **hydrocarbons**, organic compounds containing only hydrogen and carbon. The major classes of hydrocarbons are **alkanes** (formerly called paraffins), such as 2,2,3-trimethylbutane;

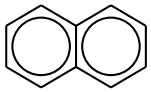


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alkenes (olefins, compounds with double bonds between adjacent carbon atoms), such as ethylene; **alkynes** (compounds with triple bonds), such as acetylene;



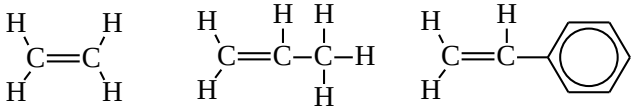
and **aromatic** (aryl) **compounds**, such as naphthalene:



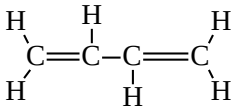
Because of their widespread use in fuels, hydrocarbons predominate among organic atmospheric pollutants. Petroleum products, primarily gasoline, are the source of most of the anthropogenic (originating through human activities) pollutant hydrocarbons found in the atmosphere. Hydrocarbons may enter the atmosphere either directly or as byproducts of the partial combustion of other hydrocarbons. The latter are particularly important because they tend to be unsaturated and relatively reactive. Most hydrocarbon pollutant sources produce about 15% reactive hydrocarbons, whereas those from incomplete combustion of gasoline are about 45% reactive. The hydrocarbons in uncontrolled automobile exhausts are only about 1/3 alkanes, with the remainder divided approximately equally between more-reactive alkenes and aromatic hydrocarbons, thus accounting for the relatively high reactivity of automotive exhaust hydrocarbons.

Alkanes are among the more stable hydrocarbons in the atmosphere. Straight-chain alkanes with 1 to more than 30 carbon atoms, and branched-chain alkanes with 6 or fewer carbon atoms, are commonly present in polluted atmospheres. Because of their high vapor pressures, alkanes with 6 or fewer carbon atoms are normally present as gases, alkanes with 20 or more carbon atoms are present as aerosols or sorbed to atmospheric particles, and alkanes with 6 to 20 carbon atoms per molecule may be present either as vapor or particles, depending upon conditions.

Alkenes enter the atmosphere from a variety of processes, including emissions from internal combustion engines and turbines, foundry operations, and petroleum refining. Several alkenes, including the ones shown below, are among the top 50 chemicals produced each year, with annual worldwide production of several billion kg:



Ethylene Propylene Styrene



Butadiene

These compounds are used primarily as monomers, which are polymerized to create polymers for plastics (polyethylene, polypropylene, polystyrene), synthetic rubber (styrenebutadiene, polybutadiene), latex paints (styrenebutadiene), and other applications. All of these compounds, as well as others manufactured in lesser quantities, are released into the atmosphere. In addition to the direct release of alkenes, these hydrocarbons are commonly produced by the partial combustion and “cracking” at

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high temperatures of alkanes, particularly in the internal combustion engine. Unlike alkanes, alkenes are highly reactive in the atmosphere, especially in the presence of NO_x and sunlight. Alkynes occur much less commonly in the atmosphere than do alkenes.

Aromatic hydrocarbons can be divided into the two major classes of those that have only one benzene ring and those with multiple rings known as *polycyclic aromatic hydrocarbons*, *PAH*. Aromatic hydrocarbons with two rings, such as naphthalene, are intermediate in their behavior. Some typical aromatic hydrocarbons are shown in Figure 16.3. The first six compounds shown in this figure are among the top 50 chemicals manufactured each year, so they are commonly encountered from pollution sources.

Polycyclic aromatic hydrocarbons are present as aerosols in the atmosphere because of their extremely low vapor pressures. These compounds are the most stable form of hydrocarbons having low hydrogen-to-carbon ratios and are formed by the combustion of hydrocarbons under oxygen-deficient conditions. The partial combustion of coal, which has a hydrogen-to-carbon ratio less than 1, is a major source of PAH compounds.

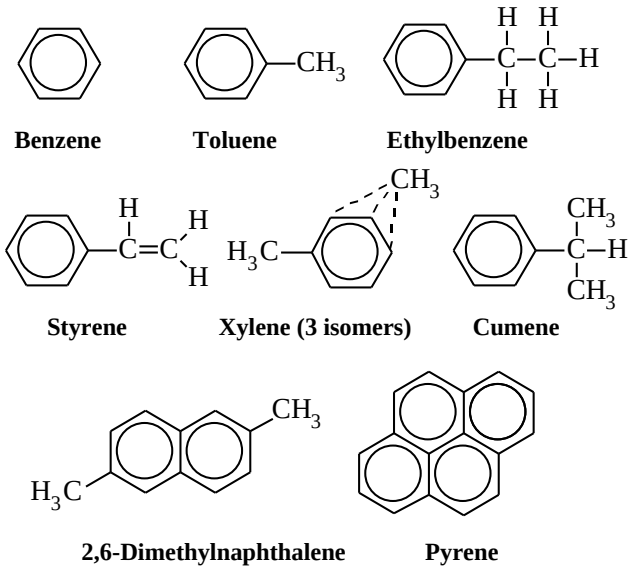


Figure 16.3 Aromatic hydrocarbons that may occur in the atmosphere. The first six compounds listed are among the top 50 chemical manufactured. The last two illustrate a bicyclic and polycyclic aromatic hydrocarbon, respectively.

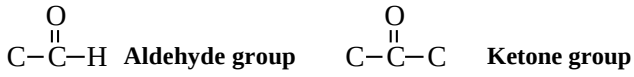
16.4 NONHYDROCARBON ORGANIC COMPOUNDS IN THE ATMOSPHERE

Carbonyl Compounds

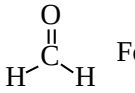
Carbonyl compounds, consisting of aldehydes and ketones that have a carbonyl moiety, C=O, are often the first species formed, other than unstable reaction intermediates, in the photochemical oxidation of atmospheric hydrocarbons. The aldehydes have the carbonyl group on an end carbon and the ketones have it on a

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carbon atom that is not at the end of a hydrocarbon chain:



The simplest and most widely produced of the carbonyl compounds is the lowest aldehyde, **formaldehyde**:


Formaldehyde

Formaldehyde is produced in the atmosphere as a product of the reaction of atmospheric hydrocarbons beginning with their reactions with hydroxyl radical, HO•. With annual global industrial production exceeding 1 billion kg, formaldehyde is used in the manufacture of plastics, resins, lacquers, dyes, and explosives. It is uniquely important because of its widespread distribution and toxicity. Humans may be exposed to formaldehyde in the manufacture and use of phenol, urea, and melamine resin plastics, and from formaldehyde-containing adhesives in pressed wood products such as particle board, used in especially large quantities in mobile home construction. However, significantly improved manufacturing processes have greatly reduced formaldehyde emissions from these synthetic building materials. Formaldehyde occurs in the atmosphere primarily in the gas phase.

The structures of some important aldehydes and ketones are shown below:

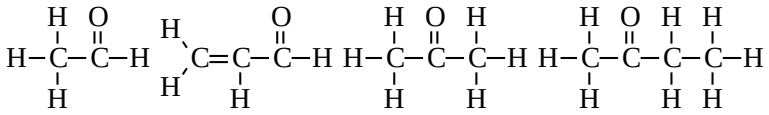


Figure 16.4 Some aldehydes and ketones that may be encoutered in the atmosphere.

Acetaldehyde is a widely produced organic chemical used in the manufacture of acetic acid, plastics, and raw materials. Approximately a billion kg of acetone are produced each year as a solvent and for applications in the rubber, leather, and plastics industries. Methylethyl ketone is employed as a low-boiling solvent for coatings and adhesives, and for the synthesis of other chemicals.

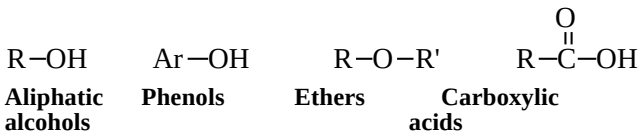
In addition to their production from hydrocarbons by photochemical oxidation, carbonyl compounds enter the atmosphere from a large number of sources and processes. These include direct emissions from internal combustion engine exhausts, incinerator emissions, spray painting, polymer manufacture, printing, petrochemicals manufacture, and lacquer manufacture. Formaldehyde and acetaldehyde are produced by microorganisms, and acetaldehyde is emitted by some kinds of vegetation.

Aldehydes are second only to NO_2 as atmospheric sources of free radicals produced by the absorption of light. This is because the carbonyl group is a **chromophore**, a molecular group that readily absorbs light. It absorbs well in the near-ultraviolet region of the spectrum to produce active species that can take part in atmospheric chemical processes.

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Miscellaneous Oxygen-Containing Compounds

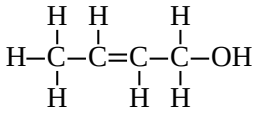
In addition to aldehydes, ketones, and esters, other oxygen-containing compounds in the atmosphere include **aliphatic alcohols**, **phenols**, **ethers**, and **carboxylic acids**. These compounds have the general formulas given below, where R and R' represent hydrocarbon moieties (groups), and Ar stands specifically for an aromatic moiety, such as the phenyl group (benzene less an H atom):



These classes of compounds include many important organic chemicals.

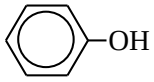
Of the alcohols, methanol, ethanol, isopropanol, and ethylene glycol rank among the top 50 chemicals with annual worldwide production of the order of a billion kg or more. The most common of the many uses of these chemicals is for the manufacture of other chemicals. Numerous aliphatic alcohols have been reported in the atmosphere. Because of their volatility, the lower alcohols, especially methanol and ethanol, predominate as atmospheric pollutants. Among the other alcohols released to the atmosphere are 1-propanol, 2-propanol, propylene glycol, 1-butanol, and even octadecanol, chemical formula $CH_3(CH_2)_{16}CH_2OH$, which is evolved by plants. Mechanisms for scavenging alcohols from the atmosphere are relatively efficient because the lower alcohols are quite water soluble and the higher ones have low vapor pressures.

Some alkenyl alcohols have been found in the atmosphere, largely as by-products of combustion. Typical of these is 2-buten-1-ol,



which has been detected in automobile exhausts. Some alkenyl alcohols are emitted by plants. One of these, *cis*-3-hexen-1-ol, $CH_3CH_2CH{=}CHCH_2CH_2OH$, is emitted from grass, trees and crop plants to the extent that it is known as “leaf alcohol.”

Phenols are aromatic alcohols that have an –OH group bonded to an aromatic ring. They are more noted as water pollutants than as air pollutants. The simplest of these compounds, phenol,

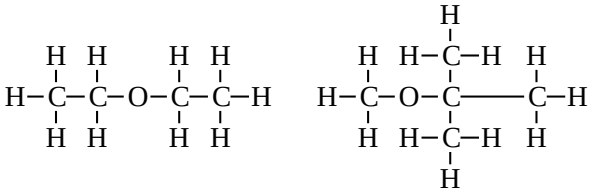


Phenol

is among the top 50 chemicals produced annually. It is most commonly used in the manufacture of resins and polymers, such as Bakelite, a phenol-formaldehyde copolymer. Phenols are produced by the pyrolysis of coal and are major byproducts of coking. Thus, in local situations involving coal coking and similar operations, phenols can be troublesome air pollutants.

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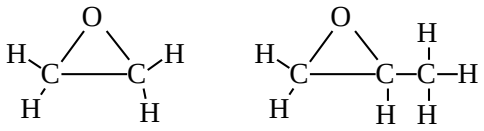
Two common ethers are diethyl ether and methyltertiarybutyl ether (MTBE) shown below:



Diethyl ether **Methyltertiarybutyl ether, MTBE**

Ethers are relatively uncommon atmospheric pollutants, although the flammability hazard of diethyl ether vapor in an enclosed work space is well known. In addition to aliphatic ethers, such as dimethyl ether and diethyl ether, several alkenyl ethers, including vinylethyl ether, are produced by internal combustion engines. Methyltertiarybutyl ether, MTBE, became the octane booster of choice to replace tetraethyllead in gasoline. Because of its widespread distribution, MTBE has the potential to be an air pollutant, although its hazard is limited by its low vapor pressure. Largely because of its potential to contaminate water, MTBE was proposed for phaseout by both the state of California and the U.S. Environmental Protection Agency in 1999. Ethers are relatively unreactive and not as water-soluble as the lower alcohols or carboxylic acids.

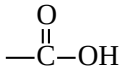
Two important organic **oxides**, ethylene oxide and propylene oxide,



Ethylene oxide **Propylene oxide**

rank among the 50 most widely produced industrial chemicals and have a limited potential to enter the atmosphere as pollutants. Ethylene oxide is a moderately to highly toxic, sweet-smelling, colorless, flammable, explosive gas used as a chemical intermediate, sterilant, and fumigant. It is a mutagen and a carcinogen to experimental animals. It is classified as hazardous for both its toxicity and ignitability.

Carboxylic acids have one or more of the functional groups,



attached to an alkane, alkene, or aryl hydrocarbon moiety. A carboxylic acid, pinonic acid, produced by the photochemical oxidation of naturally produced α-pinene, was discussed in Section 16.2. Many of the carboxylic acids found in the atmosphere probably result from the photochemical oxidation of other organic compounds through gas-phase reactions or by reactions of other organic compounds dissolved in aqueous aerosols. These acids are often the end products of photochemical oxidation because their low vapor pressures and relatively high water solubilities make them susceptible to scavenging from the atmosphere. The two lightest carboxylic acids, formic acid, HCOOH, and acetic acid, H_3CCOOH, occur commonly in the atmosphere, but are readily scavenged by precipitation because of their high water solubilities.

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Organohalides

Organohalides consisting of halogen-substituted hydrocarbon molecules, each of which contains at least one atom of F, Cl, Br, or I, may be saturated (**alkyl halides**), unsaturated (**alkenyl halides**), or aromatic (**aromatic halides**). The organohalides of environmental and toxicological concern exhibit a wide range of physical and chemical properties. Although most organohalide compounds regarded as pollutants are from anthropogenic sources, it is now known that a large variety of such compounds are generated by organisms, particularly those in marine environments.

Structural formulas of several organohalides that are potentially important in the atmosphere are shown in Figure 16.5. **Dichloromethane** is a volatile liquid with excellent solvent properties and a number of industrial uses. It is commonly employed as an extracting solvent for organic-soluble substances determined in chemical analysis. **Dichlorodifluoromethane** is one of the chlorofluorocarbon compounds once widely manufactured as a refrigerant and subsequently found to cause stratospheric ozone depletion. **Vinyl chloride** is the monomer used to manufacture huge quantities of polyvinylchloride plastics. It is a known human carcinogen. **Trichloroethylene** is a widely used solvent employed in applications such as dry cleaning. The **polychlorinated biphenyl compounds** consist of a family of compounds containing 2 aromatic rings joined as shown in the example in Figure 16.5 and containing from 1 to 10 chlorine atoms bound to the rings. The PCBs have extremely high physical and chemical stabilities and other qualities that have led to their being used in many applications, including heat transfer fluids, hydraulic fluids, and dielectrics. However, they have been banned because of their extremely high persistence and tendency to undergo bioaccumulation in the environment.

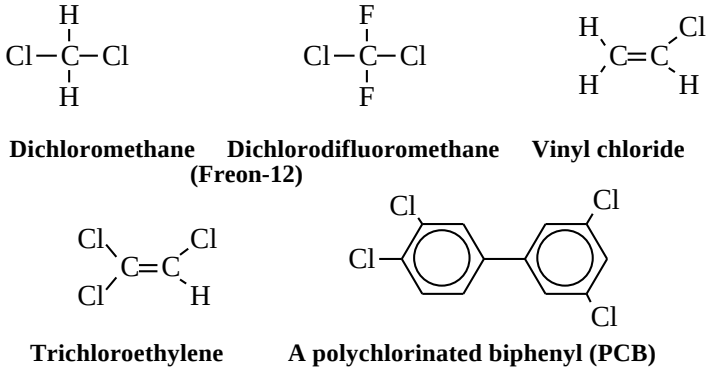


Figure 16.5 Examples of organohalide compounds that may be important in the atmosphere.

Chlorofluorocarbons and Stratospheric Ozone Depletion

Chlorofluorocarbons (**CFC**s), such as dichlorodifluoromethane, commonly called Freons, are volatile 1- and 2-carbon compounds that contain Cl and F bonded to carbon. These compounds are notably stable and nontoxic. They were widely used in recent decades in the fabrication of flexible and rigid foams and as fluids for refrigeration and air conditioning. A related class of compounds, the **halons**, such as $CBrClF_2$ (Halon-1211), are used in fire extinguisher systems particularly on aircraft.

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The nonreactivity of CFC compounds, combined with worldwide production of approximately one-half million metric tons per year and deliberate or accidental release to the atmosphere, has resulted in CFCs becoming homogeneous components of the global atmosphere. In 1974 it was convincingly suggested, in a classic work that earned the authors a Nobel Prize, that chlorofluoromethanes could catalyze the destruction of stratospheric ozone that filters out cancer-causing ultraviolet radiation from the sun. More-recent data on ozone levels in the stratosphere and on increased ultraviolet radiation at Earth's surface have shown that the threat to stratospheric ozone posed by chlorofluorocarbons is real. Although quite inert in the lower atmosphere, CFCs undergo photodecomposition by the action of high-energy ultraviolet radiation in the stratosphere, which is energetic enough to break their very strong C-Cl bonds through reactions such as

$$Cl_2CF_2 + h\nu \rightarrow Cl\bullet + ClCF_2\bullet \quad (16.4.1)$$

thereby releasing Cl atoms. The Cl atoms are very reactive species. Under the rarefied conditions of the stratosphere, one of the most abundant reactive species available for them to react with is ozone, which they destroy through a process that generates ClO:

$$Cl + O_3 \rightarrow ClO + O_2 \quad (16.4.2)$$

In the stratosphere, there is an appreciable concentration of atomic oxygen by virtue of the reaction

$$O_3 + h\nu \rightarrow O_2 + O \quad (16.4.3)$$

Nitric oxide, NO, is also present. The ClO species may react with either O or NO, regenerating Cl atoms and resulting in chain reactions that cause the net destruction of ozone:

$$ClO + O \rightarrow Cl + O_2 \quad (16.4.4)$$

$$\underline{Cl + O_3 \rightarrow ClO + O_2} \quad (16.4.5)$$

$$O_3 + O \rightarrow 2O_2 \quad (16.4.6)$$

$$ClO + NO \rightarrow Cl + NO_2 \quad (16.4.7)$$

$$\underline{O_3 + Cl \rightarrow ClO + O_2} \quad (16.4.8)$$

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (16.4.9)$$

Both ClO and Cl involved in the above chain reactions have been detected in the 25 to 45–km altitude region. Also involved as an intermediate in the stratospheric ozone destruction caused by chlorofluorocarbons is the $(ClO)_2$ dimer.

The effects of CFCs on the ozone layer may be the single greatest threat to the global atmosphere. U. S. Environmental Protection Agency regulations, imposed in accordance with the 1986 Montreal Protocol on Substances that Deplete the Ozone Layer, curtailed production of CFCs and halocarbons in the U.S. starting in 1989.

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The substitutes for these halocarbons are hydrogen-containing chlorofluorocarbons (HCFCs) and hydrogen-containing fluorocarbons (HFCs). These include CH_2FCF_3 (HFC-134a, 1,1,1,2-tetrafluoroethane, a substitute for CFC-12 in automobile air conditioners and refrigeration equipment), $CHCl_2CF_3$ (HCFC-123, substitute for CFC-11 in plastic foam-blowing), CH_3CCl_2F (HCFC-141b, substitute for CFC-11 in plastic foam-blowing) $CHClF_2$ (HCFC-22, air conditioners and manufacture of plastic foam food containers). Because of the more readily broken H-C bonds they contain, these compounds are more easily destroyed by atmospheric chemical reactions (particularly with hydroxyl radical) before they reach the stratosphere. As of 2000, the HFC 134a market was growing at about a 10 or 15% annual rate with increases of several tens of thousands of metric tons per year. This compound and related compounds containing only fluorine and hydrogen bound to carbon are favored because they cannot generate any ozone-destroying chlorine atoms.

Organosulfur Compounds

Substitution of alkyl or aryl hydrocarbon groups such as phenyl and methyl for H on hydrogen sulfide, H_2S, leads to a number of different **organosulfur thiols** (mercaptans, R–SH) and sulfides, also called thioethers (R–S–R). Structural formulas of examples of these compounds are shown in Figure 16.6. Methanethiol and other lighter alkyl thiols are fairly common air pollutants that have “ultragarlic” odors. The most significant atmospheric organosulfur compound is dimethylsulfide, produced in large quantities by marine organisms and introducing quantities of sulfur to the atmosphere comparable in magnitude to those introduced from pollution sources. Its oxidation produces most of the SO_2 in the marine atmosphere.

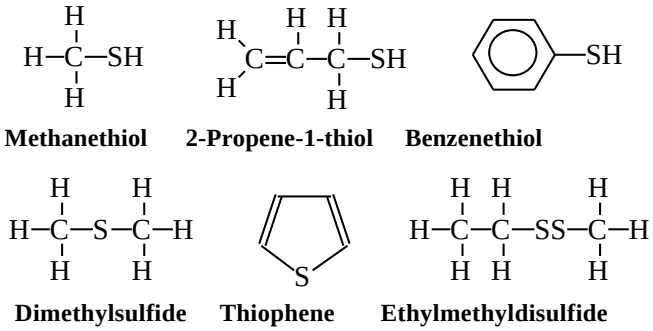


Figure 16.6 Common organosulfur compounds associated with air pollution. The organosulfur compounds are especially noted for their strong odors.

Although not highly significant as atmospheric contaminants on a large scale, organic sulfur compounds can cause local air pollution problems because of their bad odors. Major sources of organosulfur compounds in the atmosphere include microbial degradation, wood pulping, volatile matter evolved from plants, animal wastes, packing-house and rendering-plant wastes, starch manufacture, sewage treatment, and petroleum refining.

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Organonitrogen Compounds

Organic nitrogen compounds that may be found as atmospheric contaminants can be classified as **amines**, **amides**, **nitriles**, **nitro compounds**, or **heterocyclic nitrogen compounds**. Structures of common examples of each of these five classes of compounds reported as atmospheric contaminants are shown in Figure 16.7. These organonitrogen compounds can come from anthropogenic pollution sources. Significant amounts of anthropogenic atmospheric nitrogen may also come from reactions of inorganic nitrogen with reactive organic species. Examples include nitrates produced by the reaction of atmospheric NO_3.

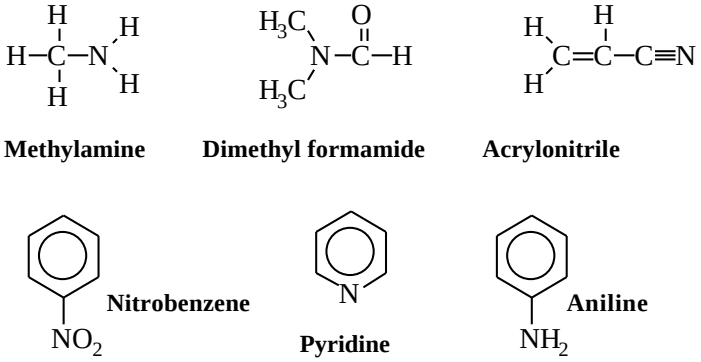


Figure 16.7 Organonitrogen compounds that may be encountered as air pollutants.

Amines consist of compounds in which one or more of the hydrogen atoms in NH_3 has been replaced by a hydrocarbon moiety. Lower-molecular-mass amines are volatile. These are prominent among the compounds giving rotten fish their characteristic odor—an obvious reason that air contamination by amines is undesirable. A number of amines are widely used industrial chemicals and solvents, so industrial sources have the potential to contaminate the atmosphere with these chemicals. Decaying organic matter, especially protein wastes, produce amines, so rendering plants, packing houses, and sewage-treatment plants are important sources of these substances. The simplest and most important aromatic amine is aniline, used in the manufacture of dyes, amides, photographic chemicals, and drugs. Although aniline is not known to be carcinogenic, some aromatic amines are of special concern as atmospheric pollutants, especially in the workplace, because some are known to cause urethral tract cancer (particularly of the bladder) in exposed individuals.

The amide most likely to be encountered as an atmospheric pollutant is dimethylformamide. It is widely used commercially as a solvent for the synthetic polymer polyacrylonitrile (Orlon, Dacron). Most amides have relatively low vapor pressures, which limit their entry into the atmosphere. Nitriles, which are characterized by the —C≡N group, have been reported as air contaminants, particularly from industrial sources. Both acrylonitrile and acetonitrile, CH_3CN, have been reported in the atmosphere as a result of synthetic rubber manufacture. Among the nitro compounds, RNO_2, reported as air contaminants are nitromethane, nitroethane, and nitrobenzene. These compounds are produced from industrial sources. Highly oxygenated compounds containing the NO_2 group, particularly

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peroxyacetyl nitrate (PAN, discussed later in this chapter), are end products of the photochemical oxidation of hydrocarbons in urban atmospheres.

16.5 PHOTOCHEMICAL SMOG

The first several pages of this chapter have discussed organic compounds in the atmosphere. The most important effects of organic pollutants on the atmosphere result from the formation of secondary pollutants characteristic of **photochemical smog**. Smog has a long history. In 1542, exploring what is now southern California, Juan Rodriguez Cabrillo named San Pedro Bay "The Bay of Smokes" because of the heavy haze that covered the area. Complaints of eye irritation from anthropogenically polluted air in Los Angeles were recorded as far back as 1868. Characterized by reduced visibility, eye irritation, cracking of rubber, and deterioration of materials, smog became a serious nuisance in the Los Angeles area during the 1940s. It is now recognized as a major air pollution problem in many areas of the world.

Smoggy conditions are manifested by moderate to severe eye irritation or visibility below 3 miles when the relative humidity is below 60%. The formation of oxidants in the air, particularly ozone, is indicative of smog formation. Serious levels of photochemical smog can be assumed to be present when the oxidant level exceeds 0.15 ppm for more than 1 hour. The three ingredients required to generate photochemical smog are ultraviolet light, hydrocarbons, and nitrogen oxides.

16.6 SMOG-FORMING AUTOMOTIVE EMISSIONS

Internal combustion engines used in automobiles and trucks produce reactive hydrocarbons and nitrogen oxides, two of the three key ingredients required for smog to form. Therefore, automotive air emissions are discussed next.

Under the conditions of high-pressure combustion in an automobile engine, elemental nitrogen and elemental oxygen react to produce nitric oxide, NO:

$$N_2 + O_2 \rightarrow 2NO \qquad (16.6.1)$$

In the absence of suitable air pollution measures, the NO produced is emitted with the exhaust gas. As discussed later in this chapter, the NO gets converted to NO_2, which is a key ingredient in the formation of photochemical smog.

At the high–temperature and –pressure conditions in an internal combustion engine, products of incompletely burned gasoline undergo chemical reactions that produce several hundred different hydrocarbons. Many of these are highly reactive in forming photochemical smog. As shown in Figure 16.8, the automobile has several potential sources of hydrocarbon emissions other than the exhaust. The first of these to be controlled was the crankcase mist of hydrocarbons composed of lubricating oil and "blowby." The latter consists of the mixture of exhaust gas and unoxidized fuel/air that enters the crankcase from the combustion chambers around the pistons. This mist is destroyed by recirculating it through the engine intake manifold by way of the positive crankcase ventilation (PCV) valve.

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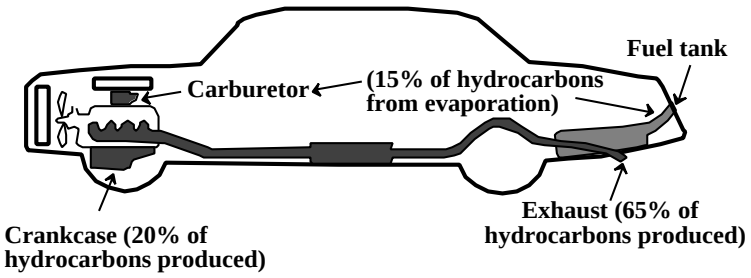


Figure 16.8 Potential sources of pollutant hydrocarbons from an automobile without pollution control devices.

A second major source of automotive hydrocarbon emissions is the fuel system, from which hydrocarbons are emitted through fuel tank and carburetor vents. When the engine is shut off and the engine heat warms up the fuel system, gasoline may be evaporated and emitted to the atmosphere. In addition, heating during the daytime and cooling at night causes the fuel tank to breathe and emit gasoline fumes. Such emissions are reduced by fuel formulated to reduce volatility. Automobiles are equipped with canisters of carbon that collect evaporated fuel from the fuel tank and fuel system, to be purged and burned when the engine is operating.

Control of Exhaust Hydrocarbons

To understand the production and control of automotive hydrocarbon exhaust products, it is helpful to understand the basic principles of the internal combustion engine. As shown in Figure 16.9, the four steps involved in one complete cycle of the four-cycle engine used in most vehicles are the following:

1. **Intake:** Air is drawn into the cylinder through the open intake valve. Gasoline is either injected with the intake air or injected separately into the cylinder.
2. **Compression:** The combustible mixture is compressed at a ratio of about 7:1. Higher compression ratios favor thermal efficiency and complete combustion of hydrocarbons. However, higher temperatures, premature combustion ("pinging"), and high production of nitrogen oxides also result from higher compression ratios.
3. **Ignition and power stroke:** As the fuel-air mixture normally produced by injecting fuel into the cylinder is ignited by the spark plug near top-dead-center, a temperature of about 2500˚C is reached very rapidly at pressures up to 40 atm. As the gas volume increases with downward movement of the piston, the temperature decreases in a few milliseconds. This rapid cooling "freezes" nitric oxide in the form of NO without allowing it time to dissociate to N_2 and O_2, which are thermodynamically favored at the normal temperatures and pressures of the atmosphere.

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4. **Exhaust:** Exhaust gases consisting largely of N_2 and CO_2, with traces of CO, NO, hydrocarbons, and O_2, are pushed out through the open exhaust valve, thus completing the cycle.

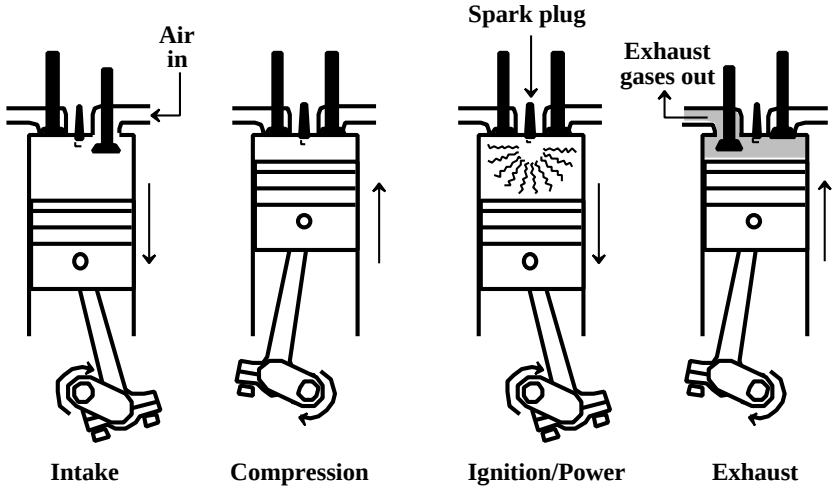


Figure 16.9 Steps in one complete cycle of a four-cycle internal combustion engine. Fuel is mixed with the intake air or injected separately into each cylinder.

The primary cause of unburned hydrocarbons in the engine cylinder is wall quench, wherein the relatively cool wall in the combustion chamber of the internal combustion engine causes the flame to be extinguished within several thousandths of a centimeter from the wall. Part of the remaining hydrocarbons may be retained as residual gas in the cylinder, and part may be oxidized in the exhaust system. The remainder is emitted to the atmosphere as pollutant hydrocarbons. Engine misfire due to improper adjustment and deceleration greatly increases the emission of hydrocarbons. Turbine engines are not subject to the wall quench phenomenon because their surfaces are always hot.

Several engine design characteristics favor lower exhaust hydrocarbon emissions. Wall quench, which is mentioned above, is diminished by design that decreases the combustion chamber surface/volume ratio through reduction of compression ratio, more nearly spherical combustion chamber shape, increased displacement per engine cylinder, and increased ratio of stroke relative to bore.

Spark retard also reduces exhaust hydrocarbon emissions. For optimum engine power and economy, the spark should be set to fire appreciably before the piston reaches the top of the compression stroke and begins the power stroke. Retarding the spark to a point closer to top-dead-center reduces the hydrocarbon emissions markedly. One reason for this reduction is that the effective surface to volume ratio of the combustion chamber is reduced, thus cutting down on wall quench. Second, when the spark is retarded, the combustion products are purged from the cylinders sooner after combustion. Therefore, the exhaust gas is hotter, and reactions consuming hydrocarbons are promoted in the exhaust system.

As shown in Figure 16.10, the air to fuel ratio in the internal combustion engine has a marked effect upon the emission of hydrocarbons. As the air to fuel ratio becomes richer in fuel than the stoichiometric ratio, the emission of hydrocarbons increases significantly. There is a moderate decrease in hydrocarbon emissions when

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the mixture becomes appreciably leaner in fuel than the stoichiometric ratio requires. The lowest level of hydrocarbon emissions occurs at an air to fuel ratio somewhat leaner in fuel than the stoichiometric ratio. This behavior is the result of a combination of factors, including minimum quench layer thickness at an air to fuel ratio somewhat richer in fuel than the stoichiometric ratio, decreasing hydrocarbon

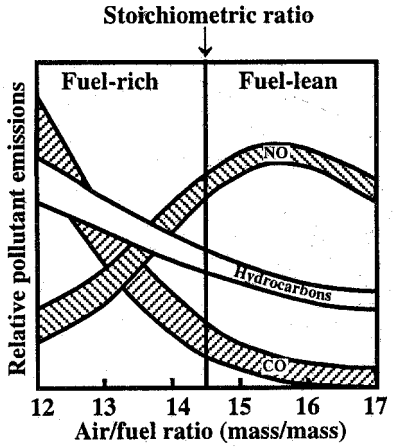


Figure 16.10 Effects of air/fuel ratio on pollutant emissions from an internal combustion piston engine.

concentration in the quench layer with a leaner mixture, increasing oxygen concentration in the exhaust with a leaner mixture, and a peak exhaust temperature at a ratio slightly leaner in fuel than the stoichiometric ratio.

Catalytic converters are now used to destroy pollutants in exhaust gases. Currently, the most commonly used automotive catalytic converter is the three-way conversion catalyst, so called because a single catalytic unit destroys all three of the main class of automobile exhaust pollutants—hydrocarbons, carbon monoxide, and nitrogen oxides. This catalyst depends upon accurate sensing of oxygen levels in the exhaust combined with computerized engine control that cycles the air to fuel mixture several times per second back and forth between slightly lean and slightly rich relative to the stoichiometric ratio. Under these conditions carbon monoxide, hydrogen, and hydrocarbons (C_cH_h) are oxidized.

$$CO + {}^1/_2O_2 \rightarrow CO_2 \tag{16.6.2}$$

$$H_2 + {}^1/_2O_2 \rightarrow H_2O \tag{16.6.3}$$

$$C_cH_h + (c + {}^h/_4)O_2 \rightarrow cCO_2 + {}^h/_2H_2O \tag{16.6.4}$$

Nitrogen oxides are reduced on the catalyst to N_2 by carbon monoxide, hydrocarbons, or hydrogen as shown by the following reduction with CO:

$$CO + NO \rightarrow {}^1/_2N_2 + CO_2 \tag{16.6.5}$$

Automotive exhaust catalysts are dispersed on a high surface area substrate, most commonly consisting of cordierite, a ceramic composed of alumina (Al_2O_3),

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silica, and magnesium oxide. The substrate is formed as a honeycomb type structure providing maximum surface area to contact exhaust gases. The support needs to be mechanically strong to withstand vibrational stresses from the automobile, and it must resist severe thermal stresses in which the temperature may rise from ambient temperatures to approximately 900˚C over an approximately two-minute period during "light-off" when the engine is started. The catalytic material, which composes only about 0.10–0.15% of the catalyst body, consists of a mixture of precious metals. Platinum and palladium catalyze the oxidation of hydrocarbons and carbon monoxide, and rhodium acts as a catalyst for the reduction of nitrogen oxides. Presently, palladium is the most common precious metal in exhaust catalysts, and as of 2000 the demand created for this element had caused its price to increase significantly.

Since lead can poison auto exhaust catalysts, automobiles equipped with catalytic exhaust-control devices require lead-free gasoline, which has become the standard motor fuel. Sulfur in gasoline is also detrimental to catalyst performance, and a controversial topic in 1999 was a proposed change in regulations to greatly decrease sulfur levels in fuel.

The internal combustion automobile engine has been developed to a remarkably high degree in terms of its emissions. The ultimate development of such an engine is one claimed to be so clean that when it is operated in a smoggy atmosphere, its exhaust is cleaner than the air that it is taking in!

The 1990 U.S. Clean Air Act called for reformulating gasoline by adding more oxygenated compounds to reduce emissions of hydrocarbons and carbon monoxide. However, this measure has been rather controversial and as noted earlier in this chapter, questions have been raised regarding one of the major oxygenated additives, methyltertiarybutyl ether, MTBE, which has become a common water pollutant in some areas.

16.7 SMOG-FORMING REACTIONS OF ORGANIC COMPOUNDS IN THE ATMOSPHERE

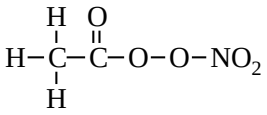
Hydrocarbons are eliminated from the atmosphere by a number of chemical and photochemical reactions. These reactions are responsible for the formation of many noxious secondary pollutant products and intermediates from relatively innocuous hydrocarbon precursors. These pollutant products and intermediates make up photochemical smog.

Hydrocarbons and most other organic compounds in the atmosphere are thermodynamically unstable toward oxidation and tend to be oxidized through a series of steps. The oxidation process terminates with formation of CO_2, solid organic particulate matter that settles from the atmosphere, or water-soluble products (for example, acids, aldehydes), which are removed by rain. Inorganic species such as ozone or nitric acid are byproducts of these reactions.

This section addresses the conditions that are characteristic of a smoggy atmosphere and the overall processes involved in smog formation. In atmospheres that receive hydrocarbon and NO pollution accompanied by intense sunlight and stagnant air masses, oxidants tend to form. In air-pollution parlance, **gross photochemical oxidant** is a substance in the atmosphere capable of oxidizing iodide ion to elemental iodine. Sometimes other reducing agents are used to measure oxidants.

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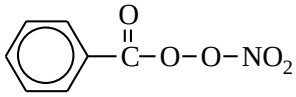
The primary oxidant in the atmosphere is ozone, O_3. Other atmospheric oxidants include H_2O_2, organic peroxides (ROOR'), organic hydroperoxides (ROOH), and peroxyacyl nitrates such as peroxyacetyl nitrate (PAN).



Peroxyacetyl nitrate (PAN)

Nitrogen dioxide, NO_2, is not regarded as a gross photochemical oxidant. However, it is about 15% as efficient as O_3 in oxidizing iodide to iodine(0), and a correction is made in measurements for the positive interference of NO_2. Sulfur dioxide is oxidized by O_3 and produces a negative interference for which a measurement correction must also be made.

Peroxyacetyl nitrate and related compounds containing the $-C(O)OONO_2$ moiety, such as peroxybenzoyl nitrate (PBN),



a powerful eye irritant and lachrymator, are produced photochemically in atmospheres containing alkenes and NO_x, and the presence of compounds of this type are important indicators of the presence of photochemical smog. PAN, especially, is a notorious organic oxidant. In addition to PAN and PBN, some other specific organic oxidants that may be important in polluted atmospheres are peroxypropionyl nitrate (PPN); peracetic acid, $CH_3(CO)OOH$; acetylperoxide, $CH_3(CO)OO(CO)CH_3$; butyl hydroperoxide, $CH_3CH_2CH_2CH_2OOH$; and *tert*-butylhydroperoxide, $(CH_3)_3COOH$.

As shown in Figure 16.11, smoggy atmospheres show characteristic variations with time of day in levels of NO, NO_2, hydrocarbons, aldehydes, and oxidants. Examination of the figure shows that, shortly after sunrise, the level of NO in the atmosphere decreases markedly, a decrease that is accompanied by a peak in the concentration of NO_2. During midday (significantly, after the concentration of NO has fallen to a very low level), the levels of aldehydes and oxidants become relatively high. The concentration of total hydrocarbons in the atmosphere peaks sharply in the morning, then decreases during the remaining daylight hours.

An overview of the processes responsible for the behavior just discussed is summarized in Figure 16.12. The chemical bases for the processes illustrated in this figure are explained in the following section.

16.8 MECHANISMS OF SMOG FORMATION

Here are discussed some of the primary aspects of photochemical smog formation. For more details the reader is referred to books on atmospheric chemistry referenced at the back of this chapter. Since the exact chemistry of photochemical smog formation is very complex, many of the reactions are given as plausible illustrative examples rather than proven mechanisms.

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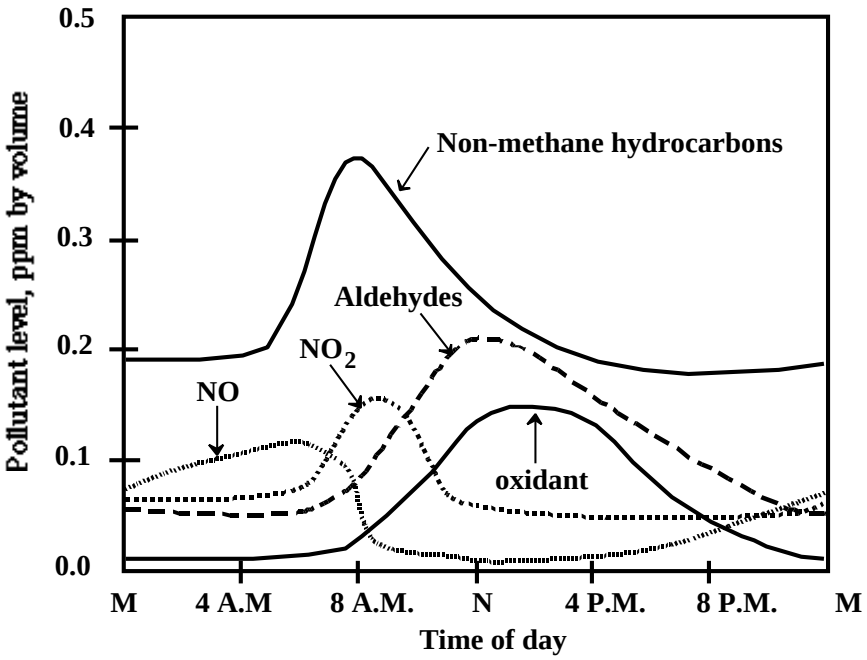


Figure 16.11 Generalized plot of atmospheric concentrations of species involved in smog formation as a function of time of day.

The kind of behavior summarized in Figure 16.11 contains several apparent anomalies that puzzled scientists for many years. The first of these was the rapid increase in NO_2 concentration and decrease in NO concentration under conditions where it was known that photodissociation of NO_2 to O and NO was occurring. Furthermore, it could be shown that the disappearance of alkenes and other hydrocarbons was much more rapid than could be explained by their relatively slow reactions with O_3 and O. These anomalies are now explained by chain reactions involving the interconversion of NO and NO_2, the oxidation of hydrocarbons, and the generation of reactive intermediates, particularly hydroxyl radical ($HO^{\bullet}$).

Figure 16.12 shows the overall reaction scheme for smog formation, which is based upon the photochemically initiated reactions that occur in an atmosphere containing nitrogen oxides, reactive hydrocarbons, and oxygen. The time variations in levels of hydrocarbons, ozone, NO, and NO_2 are explained by the following overall reactions:

1. Primary photochemical reaction producing oxygen atoms:

$$NO_2 + h\nu\ (\lambda < 420\ \text{nm}) \rightarrow NO + O \qquad (16.8.1)$$

2. Reactions involving oxygen species (M is an energy-absorbing third body):

$$O_2 + O + M \rightarrow O_3 + M \qquad (16.8.2)$$

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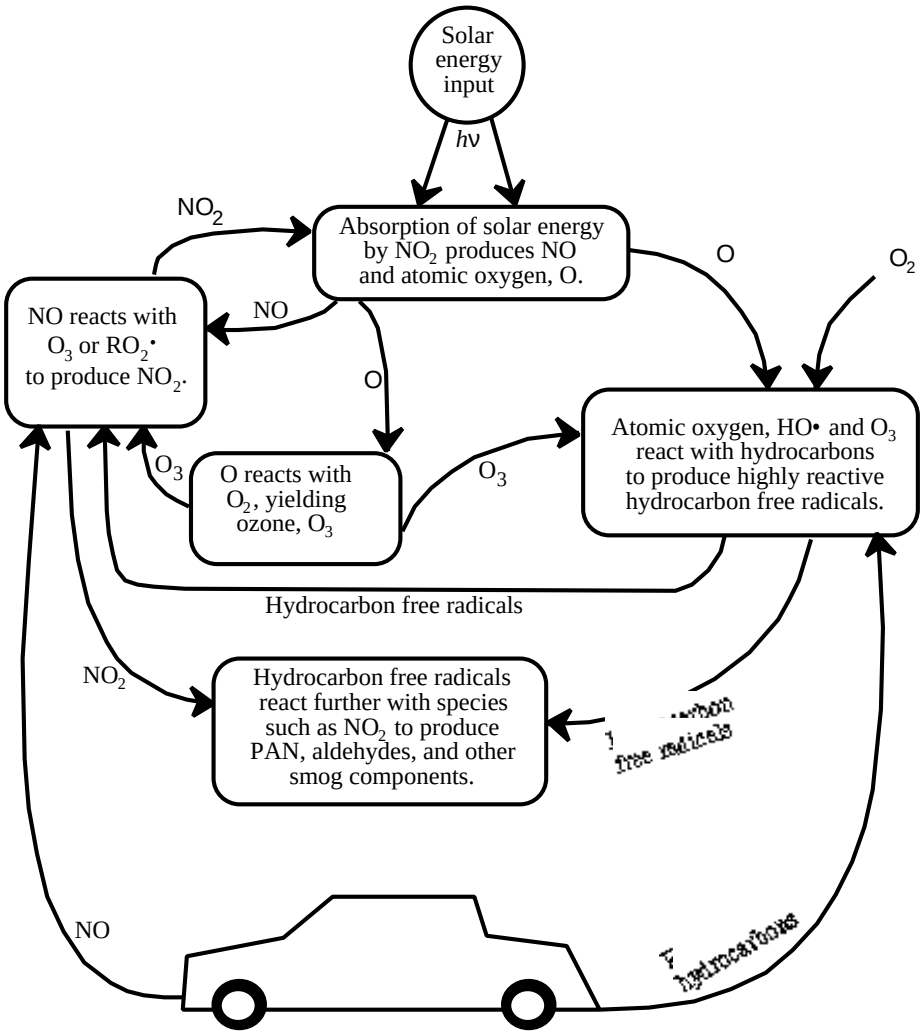


Figure 16.12 Generalized scheme for the formation of photochemical smog.

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (16.8.3)$$

3.Production of organic free radicals from hydrocarbons, RH:

$$O + RH \rightarrow R^{\bullet} + \text{other products} \qquad (16.8.4)$$

If RH in the preceding reaction were methane, CH_4, the reaction would be

$$O + CH_4 \rightarrow H_3C^{\bullet} + HO^{\bullet} \qquad (16.8.5)$$

$$O_3 + RH \rightarrow R^{\bullet} + \text{and/or other products} \qquad (16.8.6)$$

($R^{\bullet}$ is a free radical that might or might not contain oxygen.)

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4. Chain propagation, branching, and termination by a variety of reactions such as the following:

$$NO + ROO^{\bullet} \rightarrow NO_2 + \text{and/or other products} \quad (16.8.7)$$

$$NO_2 + R^{\bullet} \rightarrow \text{products (for example, PAN)} \quad (16.8.8)$$

The latter kind of reaction is the most common chain-terminating process in smog because NO_2 is a stable free radical present at high concentrations. Chains may terminate also by reaction of free radicals with NO or by reaction of two $R^{\bullet}$ radicals, although the latter is uncommon because of the relatively low concentrations of radicals compared to molecular species. Chain termination by radical sorption on a particle surface is also possible and may contribute to aerosol particle growth.

As noted at the beginning of this chapter, the key reactive intermediate species in smog formation is the very reactive $HO^{\bullet}$ radical consisting of a hydrogen and oxygen atom bonded together and with an unpaired electron on the oxygen. During the smog-forming process, hydroxyl radical is readily produced by the reaction of an oxygen atom with a hydrocarbon, as shown in Reaction 16.8.5. Hydroxyl radical can also be formed by the reaction of excited ("energized") atomic oxygen with water,

$$O^* + H_2O \rightarrow 2HO^{\bullet} \quad (16.8.9)$$

by photodissociation of hydrogen peroxide,

$$H_2O_2 + h\nu\ (\lambda < 350\ \text{nm}) \rightarrow 2HO^{\bullet} \quad (16.8.10)$$

or by the photolysis of nitrous acid,

$$HNO_2 + h\nu \rightarrow HO^{\bullet} + NO \quad (16.8.11)$$

Among the inorganic species with which the hydroxyl radical reacts are oxides of nitrogen,

$$HO^{\bullet} + NO_2 \rightarrow HNO_3 \quad (16.8.12)$$

$$HO^{\bullet} + NO + M \rightarrow HNO_2 + M \quad (16.8.13)$$

and carbon monoxide,

$$CO + HO^{\bullet} + O_2 \rightarrow CO_2 + HOO^{\bullet} \quad (16.8.14)$$

The last reaction is significant in that it is responsible for the disappearance of much atmospheric CO and because it produces the hydroperoxyl radical $HOO^{\bullet}$. One of the major inorganic reactions of the hydroperoxyl radical is the oxidation of NO:

$$HOO^{\bullet} + NO \rightarrow HO^{\bullet} + NO_2 \quad (16.8.15)$$

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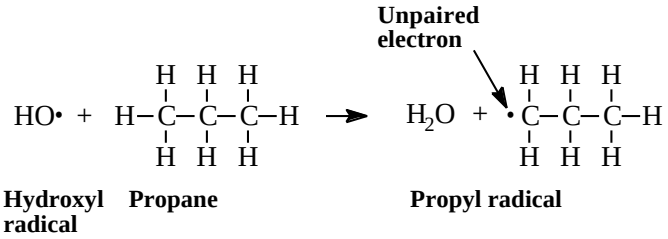
For purely inorganic systems, kinetic calculations and experimental measurements cannot explain the rapid transformation of NO to NO_2 that occurs in an atmosphere undergoing photochemical smog formation because such calculations predict that the concentration of NO_2 should remain very low. However, in the presence of reactive hydrocarbons, NO_2 accumulates very rapidly by a reaction process beginning with its photodissociation! It can be concluded, therefore, that the organic compounds form species which react with NO directly rather than with NO_2.

A number of chain reactions have been shown to result in the general type of species behavior shown in Figure 16.11. When alkane hydrocarbons, RH, react with O, O_3, or $HO^{\bullet}$ radical,

$$RH + O + O_2 \rightarrow ROO^{\bullet} + HO^{\bullet} \quad (16.8.16)$$

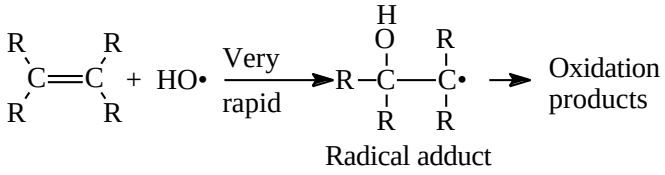
$$RH + HO^{\bullet} + O_2 \rightarrow ROO^{\bullet} + H_2O \quad (16.8.17)$$

reactive oxygenated organic radicals, $ROO^{\bullet}$, are produced. When an alkane, such as propane, reacts with a reactive species capable of removing a hydrogen atom,



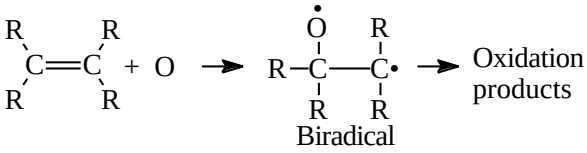
(16.8.18)

a hydrogen atom is *abstracted* from the propane and the reaction is called an **abstraction reaction**. Alkenes are much more reactive because their unsaturated carbon–carbon bonds make them capable of undergoing a second kind of reaction called an **addition reaction**:

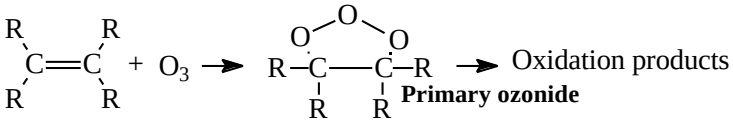


(16.8.19)

(where R may be one of a number of hydrocarbon moieties or an H atom) Alkenes may also react with oxygen atoms or with ozone as shown by the following two reactions:



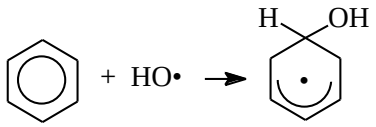
(16.8.20)



(16.8.21)

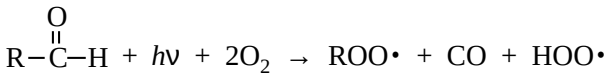
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Aromatic hydrocarbons, Ar-H, may also react with O and HO•. Addition reactions of aromatics with HO• are favored. Benzene reacts with HO• to produce a reactive radical that undergoes additional reactions involved with smog formation:

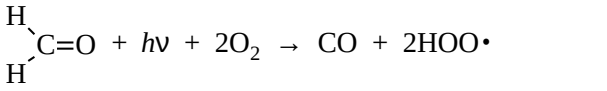


(16.8.22)

Aldehydes are strongly involved with smog formation. They may react with HO•, to produce reactive species and they can undergo direct photochemical reactions:



(16.8.23)



(16.8.24)

Hydroxyl radical (HO•), which reacts with some hydrocarbons at rates that are almost diffusion-controlled (meaning that if a molecule collides with a hydroxyl radical they react), is the predominant reactant in early stages of smog formation. Significant contributions are made by hydroperoxyl radical (HOO•) and O_3 after smog formation is well under way.

Regeneration of NO_2

One of the most important reaction sequences in the smog-formation process begins with the abstraction by HO• of a hydrogen atom from a hydrocarbon and leads to the oxidation of NO to NO_2 as follows:

$$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O \qquad (16.8.25)$$

The alkyl radical, R•, reacts with O_2 to produce a peroxyl radical, ROO•:

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \qquad (16.8.26)$$

This strongly oxidizing species very effectively oxidizes NO to NO_2,

$$ROO^{\bullet} + NO \rightarrow RO^{\bullet} + NO_2 \qquad (16.8.27)$$

thus explaining the once-puzzling rapid conversion of NO to NO_2 in an atmosphere in which the latter is undergoing photodissociation. The alkoxyl radical product, RO•, is not so stable as ROO•. In cases where the oxygen atom is attached to a carbon atom that is also bonded to H, a carbonyl compound is likely to be formed by the following type of reaction:

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$$H_3CO\bullet + O_2 \rightarrow H{-}\overset{\overset{O}{\|}}{C}{-}H + HOO\bullet \quad (16.8.28)$$

The rapid production of photosensitive carbonyl compounds from alkoxyl radicals is an important stimulant for further atmospheric photochemical reactions. In the absence of extractable hydrogen, cleavage of a radical containing the carbonyl group occurs:

$$H_3C{-}\overset{\overset{O}{\|}}{C}{-}O\bullet \rightarrow H_3C\bullet + CO_2 \quad (16.8.29)$$

Another reaction that can lead to the oxidation of NO is of the following type:

$$R{-}\overset{\overset{O}{\|}}{C}{-}OO\bullet + NO + O_2 \rightarrow ROO\bullet + NO_2 + CO_2 \quad (16.8.30)$$

Peroxyacyl nitrates are highly significant air pollutants formed by an addition reaction with NO_2:

$$R{-}\overset{\overset{O}{\|}}{C}{-}OO\bullet + NO_2 \rightarrow R{-}\overset{\overset{O}{\|}}{C}{-}OO{-}NO_2 \quad (16.8.31)$$

When R is the methyl group, CH_3, the product is peroxyacetyl nitrate, PAN. This strong oxidant is characteristic of atmospheres in which smog has been formed.

Alkyl nitrates and alkyl nitrites can be formed by the reaction of alkoxyl radicals ($RO\bullet$) with nitrogen dioxide and nitric oxide, respectively:

$$RO\bullet + NO_2 \rightarrow RONO_2 \quad (16.8.32)$$

$$RO\bullet + NO \rightarrow RONO \quad (16.8.33)$$

Addition reactions with NO_2 such as these are important in terminating the reaction chains involved in smog formation.

Nitrate Radical

First observed in the troposphere in 1980, nitrate radical, NO_3, is now recognized as being an important atmospheric chemical species, especially at night. This species is formed by the reaction

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (16.8.34)$$

and exists in equilibrium with NO_2:

$$NO_2 + NO_3 + M \leftrightarrow N_2O_5 + M \text{ (energy-absorbing third body)} \quad (16.8.35)$$

Levels of NO_3 remain low during daylight, typically with a lifetime at noon of only about 5 seconds, because of the following two dissociation reactions:

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$$NO_3 + h\nu\ (\lambda < 700\ nm) \rightarrow NO + O_2 \quad (16.8.36)$$

$$NO_3 + h\nu\ (\lambda < 580\ nm) \rightarrow NO_2 + O \quad (16.8.37)$$

However, at night the levels of NO_3 typically reach values of around 8×10^7 molecules $\times$ cm^{-3} compared with only about 1×10^6 molecules $\times$ cm^{-3} for hydroxyl radical. Although HO• reacts 10 to 1000 times faster than NO_3, the much higher concentration of NO_3 means that it is responsible for much of the atmospheric chemistry that occurs at night. The nitrate radical adds across C=C bonds in alkenes leading to the formation of reactive radical species that participate in smog formation.

Reactivity of Hydrocarbons

The reactivity of hydrocarbons in the smog formation process is an important consideration in understanding the process and in developing control strategies. It is useful to know which are the most reactive hydrocarbons so that their release can be minimized. Less-reactive hydrocarbons, of which propane is a good example, may cause smog formation far downwind from the point of release.

Hydrocarbon reactivity is best based upon the interaction of hydrocarbons with hydroxyl radical. Methane, the least-reactive common gas-phase hydrocarbon with an atmospheric half-life exceeding 10 days, is assigned a reactivity of 1.0. (Despite its low reactivity, methane is so abundant in the atmosphere that it accounts for a significant fraction of total hydroxyl radical reactions.) In contrast, β-pinene produced by conifer trees and other vegetation, is almost 9000 times as reactive as methane, and *d*-limonene, (from orange rind) is almost 19000 times as reactive.

16.9 INORGANIC PRODUCTS FROM SMOG

Two major classes of inorganic products from smog are sulfates and nitrates. Inorganic sulfates and nitrates, along with sulfur and nitrogen oxides, can contribute to acidic precipitation, corrosion, reduced visibility, and adverse health effects.

Although the oxidation of SO_2 to sulfate species is relatively slow in a clean atmosphere, it is much faster under smoggy conditions. During severe photochemical smog conditions, oxidation rates of 5–10% per hour may occur, as compared with only a fraction of a percent per hour under normal atmospheric conditions. Thus, sulfur dioxide exposed to smog can produce very high local concentrations of sulfate, which can aggravate already bad atmospheric conditions.

Several oxidant species in smog can oxidize SO_2. Among the oxidants are compounds, including O_3, NO_3, and N_2O_5, as well as reactive radical species, particularly HO•, HOO•, O, RO•, and ROO•. The two major primary reactions are oxygen transfer,

$$SO_2 + O\ (\text{from O, RO•, ROO•}) \rightarrow SO_3 \rightarrow H_2SO_4, \text{sulfates} \quad (16.9.1)$$

or addition. As an example of the latter, HO• adds to SO_2 to form a reactive species that can further react with oxygen, nitrogen oxides, or other species to yield sulfates, other sulfur compounds, or compounds of nitrogen:

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$$HO^{\bullet} + SO_2 \rightarrow HOSOO^{\bullet} \quad (16.9.2)$$

The presence of $HO^{\bullet}$ (typically at a level of 3×10^6 radicals/cm^3, but appreciably higher in a smoggy atmosphere) makes this a likely route. Addition of SO_2 to $RO^{\bullet}$ or $ROO^{\bullet}$ can yield organic sulfur compounds.

It should be noted that the reaction of H_2S with $HO^{\bullet}$ is quite rapid. As a result, the normal atmospheric half-life of H_2S of about one-half day becomes much shorter in the presence of photochemical smog.

Inorganic nitrates or nitric acid are formed by several reactions in smog. Among the important reactions forming HNO_3 are the reaction of N_2O_5 with water and the addition of hydroxyl radical to NO_2. The oxidation of NO or NO_2 to nitrate species may occur after absorption of gas by an aerosol droplet. Nitric acid formed by these reactions reacts with ammonia in the atmosphere to form ammonium nitrate:

$$NH_3 + HNO_3 \rightarrow NH_4NO_3 \quad (16.9.3)$$

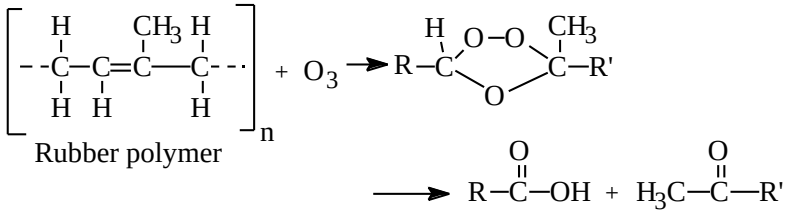
Other nitrate salts may also be formed.

Nitric acid and nitrates are among the more damaging end products of smog. In addition to possible adverse effects on plants and animals, they cause severe corrosion problems. Electrical relay contacts and small springs associated with electrical switches are especially susceptible to damage from nitrate-induced corrosion.

16.10 EFFECTS OF SMOG

The harmful effects of smog occur mainly in the areas of (1) human health and comfort, (2) damage to materials, (3) effects on the atmosphere, and (4) toxicity to plants. The exact degree to which exposure to smog affects human health is not known, although substantial adverse effects are suspected. Pungent-smelling, smog-produced ozone is known to be toxic. Ozone at 0.15 ppm causes coughing, wheezing, bronchial constriction, and irritation to the respiratory mucous system in healthy, exercising individuals. In addition to ozone, oxidant peroxyacyl nitrates and aldehydes found in smog are eye irritants.

Materials are adversely affected by some smog components. Rubber has a high affinity for ozone and is cracked and aged by it. Indeed, the cracking of rubber used to be employed as a test for the presence of ozone. Ozone attacks natural rubber and similar materials by oxidizing and breaking double bonds in the polymer according to the following reaction:



(16.10.1)

This oxidative scission type of reaction causes bonds in the polymer structure to break and results in deterioration of the polymer.

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Aerosol particles that reduce visibility are formed by the polymerization of the smaller molecules produced in smog-forming reactions. Since these reactions largely involve the oxidation of hydrocarbons, it is not suprising that oxygen-containing organics make up the bulk of the particulate matter produced from smog. Ether-soluble aerosols collected from the Los Angeles atmosphere have shown an empirical formula of approximately CH_2O. Among the specific kinds of compounds identified in organic smog aerosols are alcohols, aldehydes, ketones, organic acids, esters, and organic nitrates. Hydrocarbons of plant origin are prominent among the precursors to particle formation in photochemical smog.

Smog aerosols likely form by condensation on existing nuclei rather than by self-nucleation of smog reaction product molecules. In support of this view are electron micrographs of these aerosols showing that smog aerosol particles in the micrometer-size region consist of liquid droplets with an inorganic electron-opaque core (Figure 16.13). Thus, particulate matter from a source other than smog may have some influence on the formation and properties of smog aerosols.

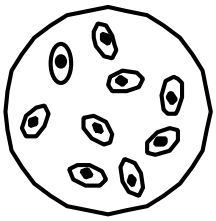


Figure 16.13 Representation of an electron micrograph of smog aerosol particles collected by a jet inertial impactor, showing electron-opaque nuclei in the centers of the impacted droplets.

In view of worldwide shortages of food, the known harmful effects of smog on plants is of particular concern. These effects are largely due to oxidants in the smoggy atmosphere. The three major oxidants involved are ozone, PAN, and nitrogen oxides. Of these, PAN has the highest toxicity to plants, attacking younger leaves and causing “bronzing” and “glazing” of their surfaces. Exposure for several hours to an atmosphere containing PAN at a level of only 0.02–0.05 ppm will damage vegetation. The sulfhydryl group of proteins in organisms is susceptible to damage by PAN, which reacts with such groups as both an oxidizing agent and an acetylating agent. Fortunately, PAN is usually present at only low levels. Nitrogen oxides occur at relatively high concentrations during smoggy conditions, but their toxicity to plants is relatively low.

Short-chain alkyl hydroperoxides, which were mentioned in Section 16.7, occur at low levels under smoggy conditions, and even in remote atmospheres. It is possible that these species can oxidize DNA bases, causing adverse genetic effects. Alkyl hydroperoxides are formed under smoggy conditions by the reaction of alkyl peroxy radicals with hydroperoxy radical, $HO_2^{\bullet}$, as shown for the formation of methyl hydroperoxide below:

$$H_3CO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_3COOH + O_2 \qquad (16.10.2)$$

Ames assays of methyl, ethyl, *n*-propyl, and *n*-butyl hydroperoxides (see Chapter 23) have shown some tendency toward mutagenicity on select strains of *Salmonella typhimurium*, although any conclusions drawn from such studies on human health

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should be made with caution.

The low toxicity of nitrogen oxides and the usually low levels of PAN, hydroperoxides, and other oxidants present in smog leave ozone as the greatest smog-produced threat to plant life. Some plant species, including sword-leaf lettuce, black nightshade, quickweed, and double-fortune tomato, are so susceptible to the effects of ozone and other photochemical oxidants that they are used as bioindicators of the presence of smog. Typical of the phytotoxicity of O_3, ozone damage to a lemon leaf is typified by chlorotic stippling (characteristic yellow spots on a green leaf), as represented in Figure 16.14. Reduction in plant growth may occur without visible lesions on the plant.

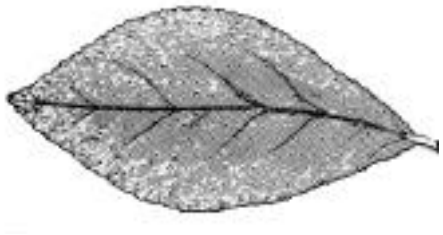


Figure 16.14 Representation of ozone damage to a lemon leaf. In color, the spots appear as yellow chlorotic stippling on the green upper surface caused by ozone exposure.

Brief exposure to approximately 0.06 ppm of ozone may temporarily cut photosynthesis rates in some plants in half. Crop damage from ozone and other photochemical air pollutants in California alone is estimated to cost millions of dollars each year. The geographic distribution of damage to plants in California is illustrated in Figure 16.15.



Figure 16.15 Geographic distribution of plant damage from smog in California.

Good News About Smog

Measures to control smog continue to be notably successful in Los Angeles, the city most commonly associated with high smog levels in the U.S. This is illustrated in Figure 16.16, which shows the number of days per year in which levels of ozone, the air pollutant most associated with photochemical smog, have exceeded federal standards of 120 parts per billion by volume (ppbv) for at least 1 hour during the

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day. This figure shows that the number of days each year in which this level was exceeded reached 180 in 1988. Since then, the days per year exceeding the 120 ppbv level have decreased steadily to current values of fewer than 60 days per year.

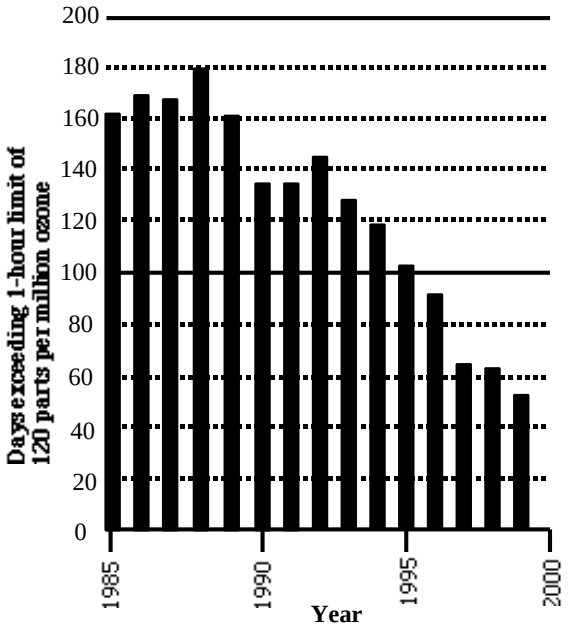


Figure 16.16 Days each year in which ozone levels have exceeded 120 ppbv, indicating a distinct downward trend in the occurrence of photochemical smog in Los Angeles. Based upon data from the U.S. Environmental Protection Agency.

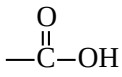
CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

The effects of organic pollutants in the atmosphere can be broadly divided between [1]_____ and [2]_____ _____. Global distillation and fractionation of persistent organic pollutants has the effect of [3]_____ _____. In considering reactions and fates of organic pollutants, the symbols $h\nu$ represent [4]_____, which can be absorbed by a molecule, and the most important reactive intermediate species is [5]_____. Of total hydrocarbons in the atmosphere only about [6]_____ come from human activities, largely because of the huge amounts of [7]_____ generated from natural sources. Most of the hydrocarbons emitted by plants are [8]_____, which come from plants such as [9]_____. The three major classes of pollutant hydrocarbons are [10]_____ _____ of which [11]_____ are the most reactive because of

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their [12]_____ Frequently **t**he first species formed, other than unstable reaction intermediates, in the photochemical oxidation of atmospheric hydrocarbons are [13]_____, which may be either [14]_____ _____. The simplest and most widely produced of the carbonyl compounds and the one most commonly encountered in the atmosphere is [15]_____ _____. The lighter alcohols are readily removed from the atmosphere because of [16]_____. An ether used as a gasoline additive is [17]_____. Compounds with an oxygen atom bridging between two carbons are [18]_____ and those containing the



group are [19]_____. An organohalide that is a known human carcinogen is [20]_____, the class of organohalides shown to be damaging to the stratospheric ozone layer consists of the [21]_____, and extremely stable organohalides containing two aromatic rings, now banned because of their environmental persistence, are the [22]_____, The compounds developed to substitute for the ozone depleting organohalides mentioned above all contain [23]_____.
The alkyl thiols belong to the general class of [24]_____ compounds and are noted for their [25]_____. Compounds noted for their rotten fish odors are the [26]_____. Conditions under which photochemical smog is present are manifested by [27]_____ _____.
The three ingredients required to generate photochemical smog are [28]_____. _____.
In addition to hydrocarbons, a compound involved in photochemical smog formation that is emitted by internal combustion (automobile) engines is [29]_____. The device now used to destroy smog-forming pollutants from automobile engines once they have been generated by the engine is the [30]_____.
A driving force behind photochemical smog formation is that hydrocarbons and most other organic compounds in the atmosphere are [31]_____ _____ and tend to be [32]_____ through a series of steps. A simple inorganic oxidant characteristic of the presence of photochemical smog is [33]_____ and a strongly oxidizing organic compound containing N is [34]_____. Two kinds of behavior that puzzled early investigators of the smog-forming process are [35]_____ _____ _____.
The initial photochemical reaction that initiates smog formation is [36]_____ _____. A reaction between a hydrocarbon, RH, and an oxygen atom that produces two free radicals, one of which is the most significant reactive intermediate species in the smog-forming process is [37]_____ _____. A reaction of one of the products of this reaction with O_2 that generates a species that completes a key part of the cyclic process that keeps smog formation underway is [38]_____.
A common reaction of $HO^{\bullet}$ that removes this radical from the atmosphere and produces an inorganic acid is [39]_____. The main

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reaction that alkanes can undergo with O atoms or HO• radical is the [40]_____ _____ reaction, whereas alkenes can also undergo [41]_____ reactions. Alkenes can react with [42]_____ to produce a species in which 3 O atoms are bridged between 2 C atoms. The first class of stable, though reactive, species formed during the oxidation of hydrocarbons during smog formation consists of [43]_____ which, unlike most common organic compounds in the atmosphere can undergo direct [44]_____. The fact that hydroxyl radical reacts with some hydrocarbons at rates that are almost diffusion-controlled means that [45]_____ _____. A reactive species in the atmosphere that is especially important at night is [46]_____. Hydrocarbon reactivity is commonly based upon the interaction of hydrocarbons with [47]_____ _____. The least reactive common hydrocarbon is [48]_____. A hydrocarbon from conifer trees that is 9000 times as reactive is [49]_____. Two major classes of inorganic products from smog are [50]_____, which have the effects of [51]_____ _____. The harmful effects of smog occur mainly in the four areas of [52]_____ _____. Ozone adversely affects rubber by [53]_____. The three major oxidants that adversely affect plants are [54]_____ _____. From the late 1980s until about 2000, the number of days that Los Angeles air has exceeded the 120 ppbv ozone standard has dropped from [55]_____ to around [56]_____.

Answers to Chapter Summary

1. direct effects
2. effects from the formation of secondary pollutants
3. depositing such pollutants in colder polar or mountainous regions
4. a photon of energy from electromagnetic radiation
5. hydroxyl radical, HO•
6. 1/7
7. methane
8. terpenes
9. conifers and those of the genus *Myrtus*
10. alkanes, alkenes, and aromatic compounds
11. alkenes
12. C=C double bonds
13. carbonyl compounds
14. aldehydes or ketones
15. formaldehyde
16. their high water solubility
17. methyltertiarybutyl ether, MTBE
18. oxides
19. carboxylic acids
20. vinyl chloride
21. chlorofluorocarbons (Freons)

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22. polychlorinated biphenyls (PCBs)
23. more readily broken C-H bonds
24. organosulfur compounds
25. terrible odors
26. lower molecular mass amines
27. moderate to severe eye irritation or visibility below 3 miles when the relative humidity is below 60%
28. ultraviolet light, hydrocarbons, and nitrogen oxides
29. NO
30. three-way conversion catalyst
31. thermodynamically unstable toward oxidation
32. oxidized
33. ozone, O_3
34. peroxyacetyl nitrate, PAN
35. the rapid increase in NO_2 concentration and decrease in NO concentration and the disappearance of alkenes and other hydrocarbons much faster than could be explained by their relatively slow reactions with O_3 and O
36. $NO_2 + h\nu\ (\lambda < 420\ nm) \rightarrow NO + O$
37. $RH + O \rightarrow R\bullet + HO\bullet$
38. $RO_2\bullet + NO \rightarrow RO\bullet + NO_2$ (regeneration of photolyzable NO_2)
39. $HO\bullet + NO_2 \rightarrow HNO_3$
40. abstraction
41. addition
42. ozone
43. aldehydes
44. photochemical reactions
45. whenever a species collides with a hydroxyl radical, it reacts
46. nitrate radical NO_3
47. hydroxyl radical
48. methane
49. β-pinene
50. sulfates and nitrates
51. contributing to acidic precipitation, corrosion, reducing visibility, and adverse health effects
52. (1) human health and comfort, (2) damage to materials, (3) effects on the atmosphere, and (4) toxicity to plants
53. cracking and aging it
54. ozone, PAN, and nitrogen oxides
55. 180
56. 50

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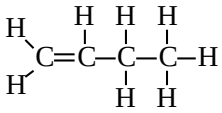
QUESTIONS AND PROBLEMS

1. Match each organic pollutant in the left column with its expected effect in the right column, below:

A. CH_3SH	1. Most likely to have a secondary effect in the atmosphere

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B. $CH_3CH_2CH_2CH_3$ 2. Most likely to have a direct effect

C.  3. Should have the least effect of these three

2. Why are hydrocarbon emissions from uncontrolled automobile exhaust particularly reactive?
3. Assume an accidental release of a mixture of gaseous alkanes and alkenes into an urban atmosphere early in the morning. If the atmosphere at the release site is monitored for these compounds, what can be said about their total and relative concentrations at the end of the day? Explain.
4. Match each radical in the left column with its type in the right column, below:

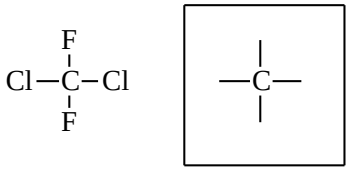
A. $H_3C^{\bullet}$	1. Formyl radical
B. $CH_3CH_2O^{\bullet}$	2. Alkylperoxyl radical
C. $\overset{\bullet}{H}CO$	3. Alkyl radical
D. $CH_xCH_{2x+1}O_2^{\bullet}$	4. Alkoxyl radical

5. When reacting with hydroxyl radical, alkenes have a reaction mechanism not available to alkanes, which makes the alkenes much more reactive. What is this mechanism?
6. What is the most stable type of hydrocarbon that has a very low hydrogen-to-carbon ratio?
7. In the sequence of reactions leading to the oxidation of hydrocarbons in the atmosphere, what is the first stable class of compounds generally produced?
8. Give a sequence of reactions leading to the formation of acetaldehyde from ethane starting with the reaction of hydroxyl radical.
9. What important photochemical property do carbonyl compounds share with NO_2?
10. Of the following species, the one that is the least likely product of the absorption of a photon of light by a molecule of NO_2 is: (a) O, (b) a free radical species, (c) NO, (d) NO_2*, (e) N atoms.
11. Which of the following statements is true: (a) $RO^{\bullet}$ reacts with NO to form alkyl nitrates, (b) $RO^{\bullet}$ is a free radical, (c) $RO^{\bullet}$ is not a very reactive species, (d) $RO^{\bullet}$ is readily formed by the action of stable hydrocarbons and ground state NO_2, (e) $RO^{\bullet}$ is not thought to be an intermediate in the smog-forming process.
12. Of the following species, the one most likely to be found in reducing smog is: ozone, relatively high levels of atomic oxygen, SO_2, PAN, PBN.
13. Why are automotive exhaust pollutant hydrocarbons even more damaging to the environment than their quantities would indicate?
14. At what point in the smog-producing chain reaction is PAN formed?
15. What particularly irritating product is formed in the laboratory by the irradiation

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of a mixture of benzaldelhyde and NO_2 with ultraviolet light?

16. Which of the following species reaches its peak value last on a smog-forming day: NO, oxidants, hydrocarbons, NO_2?
17. What is the main species responsible for the oxidation of NO to NO_2 in a smoggy atmosphere?
18. Give two reasons that a turbine engine should have lower hydrocarbon emissions than an internal combustion engine.
19. What pollution problem does a lean mixture aggravate when employed to control hydrocarbon emissions from an internal combustion engine?
20. Why is a modern automotive catalytic converter called a "three-way conversion catalyst?"
21. What is the distinction between *reactivity* and *instability* as applied to some of the chemically active species in a smog-forming atmosphere?
22. Why might carbon monoxide be chosen as a standard against which to compare automotive hydrocarbon emissions in atmospheres where smog is formed? What are some pitfalls created by this choice?
23. What is the purpose of alumina in an automotive exhaust catalyst? What kind of material actually catalyzes the destruction of pollutants in the catalyst?
24. The compound on the left, below, is one that has some useful properties and has been widely produced, but which has one potentially very detrimental effect on the environment. In the box, give the formula of a compound that might have similar beneficial properties, but would not pose the same environmental threat.

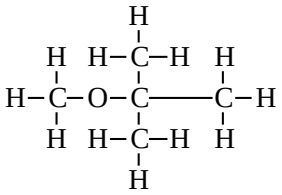


25. How might oxidants be detected in the atmosphere?
26. Why is ozone especially damaging to rubber?
27. Show how hydroxyl radical, $HO^{\bullet}$, might react differently with ethylene, $H_2C{=}CH_2$, and methane, CH_4.
28. Indicate, with reasons for the choice, which of the following is likely to be **least** reactive: Benzene, ethylene, *d*-limonene, β-pinene.
29. Of the following regarding organic air pollutants, the true statement is

 A. Carbonyl compounds (aldehydes and ketones) are usually the last organic species formed during the photochemical oxidation of hydrocarbons.
 B. Carboxylic acids (containing the $-CO_2H$ group) are especially long-lived and persistent in the atmosphere.
 C. The compound below is a potential air pollutant because it is widely

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manufactured and distributed.



D. Chlorofluorocarbons, such as CCl_2F_2, are secondary pollutants.
E. Peroxyacetyl nitrate, PAN, is a primary pollutant.

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17 THE GEOSPHERE AND GEOCHEMISTRY

17.1 INTRODUCTION

The **geosphere**, or solid earth, is that part of the earth upon which humans live and from which they extract most of their food, minerals, and fuels. Once thought to have an almost unlimited buffering capacity against the perturbations of humankind, the geosphere is now known to be rather fragile and subject to harm by human activities. For example, some billions of tons of earth material are mined or otherwise disturbed each year in the extraction of minerals and coal. Two atmospheric pollutant phenomena—excess carbon dioxide and acid rain (see Chapter 15)—have the potential to cause major changes in the geosphere. Too much carbon dioxide in the atmosphere may cause global heating ("greenhouse effect"), which could significantly alter rainfall patterns and turn currently productive areas of the earth into desert regions. The low pH characteristic of acid rain can bring about drastic changes in the solubilities and oxidation-reduction rates of minerals. Erosion caused by intensive cultivation of land is washing away vast quantities of topsoil from fertile farmlands each year. In some areas of industrialized countries, the geosphere has been the dumping ground for toxic chemicals. Ultimately, the geosphere must provide disposal sites for the nuclear wastes of the more than 400 nuclear reactors that have operated worldwide. It may be readily seen that the preservation of the geosphere in a form suitable for human habitation is one of the greatest challenges facing humankind.

The interface between the geosphere and the atmosphere at Earth's surface is very important to the environment. Human activities on the earth's surface may affect climate, most directly through the change of surface albedo, defined as the percentage of incident solar radiation reflected by a land or water surface. For example, if the sun radiates 100 units of energy per minute to the outer limits of the atmosphere, and the earth's surface receives 60 units per minute of the total, then reflects 30 units upward, the albedo is 50 percent. Some typical albedo values for different areas on the earth's surface are: evergreen forests, 7–15%; dry, plowed

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fields, 10–15%; deserts, 25–35%; fresh snow, 85–90%; asphalt, 8%. In some heavily developed areas, anthropogenic (human-produced) heat release is comparable to the solar input. The anthropogenic energy release over the 60 square kilometers of Manhattan Island averages about 4 times the solar energy falling on the area; over the 3500 km^2 of Los Angeles, the anthropogenic energy release is about 13% of the solar flux.

One of the greater impacts of humans upon the geosphere is the creation of desert areas through abuse of land that has marginal amounts of rainfall. This process, called **desertification**, is manifested by declining groundwater tables, salinization of topsoil and water, reduction of surface waters, unnaturally high soil erosion, and desolation of native vegetation. The problem is severe in some parts of the world, particularly Africa's Sahel (southern rim of the Sahara), where the Sahara advanced southward at a particularly rapid rate during the period 1968–73, contributing to widespread starvation in Africa during the 1980s. Large arid areas of the western U.S. are experiencing at least some desertification as the result of human activities and a severe drought during the latter 1980s and early 1990s. As the populations of the western states increase, one of the greatest challenges facing the residents is to prevent additional conversion of land to desert.

The most important part of the geosphere for life on earth is soil. It is the medium upon which plants grow, and virtually all terrestrial organisms depend upon it for their existence. The productivity of soil is strongly affected by environmental conditions and pollutants. Because of the importance of soil, all of Chapter 16 is devoted to its environmental chemistry.

With increasing population and industrialization, one of the more important aspects of human use of the geosphere has to do with the protection of water sources. Mining, agricultural, chemical, and radioactive wastes all have the potential for contaminating both surface water and groundwater. Sewage sludge spread on land may contaminate water by release of nitrate and heavy metals. Landfills may likewise be sources of contamination. Leachates from unlined pits and lagoons containing hazardous liquids or sludges may pollute drinking water.

It should be noted, however, that many soils have the ability to assimilate and neutralize pollutants. Various chemical and biochemical phenomena in soils operate to reduce the harmful nature of pollutants. These phenomena include oxidation-reduction processes, hydrolysis, acid-base reactions, precipitation, sorption, and biochemical degradation. Some hazardous organic chemicals may be degraded to harmless products on soil, and heavy metals may be sorbed by it. In general, however, extreme care should be exercised in disposing of chemicals, sludges, and other potentially hazardous materials on soil, particularly where the possibility of water contamination exists.

17.2 THE NATURE OF SOLIDS IN THE GEOSPHERE

The earth is divided into layers, including the solid iron-rich inner core, molten outer core, mantle, and crust. Environmental chemistry is most concerned with the **lithosphere**, which consists of the outer mantle and the **crust**. The latter is the earth's outer skin that is accessible to humans. It is extremely thin compared with the diameter of the earth, ranging from 5 to 40 km thick.

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Most of the solid earth crust consists of rocks. Rocks are composed of minerals, where a **mineral** is a naturally occurring inorganic solid with a definite internal crystal structure and chemical composition. A **rock** is a solid, cohesive mass of pure mineral or an aggregate of two or more minerals.

Structure and Properties of Minerals

The combination of two characteristics is unique to a particular mineral. These characteristics are a defined chemical composition, as expressed by the mineral's chemical formula, and a specific crystal structure. The **crystal structure** of a mineral refers to the way in which the atoms are arranged relative to each other. It cannot be determined from the appearance of visible crystals of the mineral, but requires structural methods such as X-ray structure determination. Different minerals may have the same chemical composition, or they may have the same crystal structure, but cannot have both the identical for truly different minerals.

Physical properties of minerals can be used to classify them. The characteristic external appearance of a pure crystalline mineral is its **crystal form**. Because of space constrictions on the ways that minerals grow, the pure crystal form of a mineral is often not expressed. **Color** is an obvious characteristic of minerals, but can vary widely due to the presence of impurities. The appearance of a mineral surface in reflected light describes its **luster**. Minerals may have a metallic luster or appear partially metallic (or submetallic), vitreous (like glass), dull or earthy, resinous, or pearly. The color of a mineral in its powdered form as observed when the mineral is rubbed across an unglazed porcelain plate is known as **streak**. **Hardness** is expressed on Mohs scale, which ranges from 1 to 10 and is based upon 10 minerals that vary from talc, hardness 1, to diamond, hardness 10. **Cleavage** denotes the manner in which minerals break along planes and the angles in which these planes intersect. For example, mica cleaves to form thin sheets. Most minerals **fracture** irregularly, although some fracture along smooth curved surfaces or into fibers or splinters. **Specific gravity**, density relative to that of water, is another important physical characteristic of minerals.

Kinds of Minerals

Although over 2000 minerals are known, only about 25 **rock-forming minerals** make up most of the earth's crust. The nature of these minerals can be better understood with a knowledge of the elemental composition of the crust. Oxygen and silicon make up 49.5% and 25.7% by mass of the earth's crust, respectively. Therefore, most minerals are **silicates** such as quartz, SiO_2, or orthoclase, $KAlSi_3O_8$. In descending order of abundance, the other elements in the earth's crust are aluminum (7.4%), iron (4.7%), calcium (3.6%), sodium (2.8%), potassium (2.6%), magnesium (2.1%), and "other (1.6%)". Table 17.1 summarizes the major kinds of minerals in the earth's crust.

Secondary minerals are formed by alteration of parent mineral matter. **Clays** are silicate minerals, usually containing aluminum, which constitute one of the most significant classes of secondary minerals. Olivine, augite, hornblende, and feldspars all form clays. Clays are discussed in detail in Section 17.7.

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Table 17.1 Major Mineral Groups in the Earth's Crust

Mineral group	Examples	Formula
Silicates	Quartz	SiO_2
	Olivine	$(Mg,Fe)_2SiO_4$
	Potassium feldspar	$KAlSi_3O_8$
Oxides	Corundum	Al_2O_3
	Magnetite	Fe_3O_4
Carbonates	Calcite	$CaCO_3$
	Dolomite	$CaCO_3 \cdot MgCO_3$
Sulfides	Pyrite	FeS_2
	Galena	PbS
Sulfates	Gypsum	$CaSO_4 \cdot 2H_2O$
Halides	Halite	NaCl
	Fluorite	CaF_2
Native elements	Copper	Cu
	Sulfur	S

Evaporites

Evaporites are soluble salts that precipitate from solution under special arid conditions, commonly as the result of the evaporation of seawater. The most common evaporite is **halite**, NaCl. Other simple evaporite minerals are sylvite (KCl), thenardite (Na_2SO_4), and anhydrite ($CaSO_4$). Many evaporites are hydrates, including bischofite ($MgCl_2 \cdot 6H_2O$), kieserite ($MgSO_4 \cdot H_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), and epsomite ($MgSO_4 \cdot 7H_2O$). Double salts, such as carnallite ($KMgCl_3 \cdot 6H_2O$), polyhalite ($K_2MgCa_2(SO_4)_4 \cdot 2H_2O$), kainite ($KMgClSO_4 \cdot {}^{11}/_4H_2O$), glaserite ($K_3Na(SO_4)_2$), and loeweite ($Na_{12}Mg_7(SO_4)_{13} \cdot 15H_2O$), are very common in evaporites.

The precipitation of evaporites from marine and brine sources depends upon a number of factors. Prominent among these are the concentrations of the evaporite ions in the water and the solubility products of the evaporite salts. The presence of a common ion decreases solubility; for example, $CaSO_4$ precipitates more readily from a brine that contains Na_2SO_4 than it does from a solution that contains no other source of sulfate. The presence of other salts that do not have a common ion increases solubility because it decreases activity coefficients. Differences in temperature result in significant differences in solubility.

The nitrate deposits that occur in the hot and extraordinarily dry regions of northern Chile are chemically unique because of the stability of highly oxidized nitrate salts. The dominant salt, which has been mined for its nitrate content for use

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in explosives and fertilizers, is Chile saltpeter, $NaNO_3$. Traces of highly oxidized $CaCrO_4$ and $Ca(ClO_4)_2$ are also encountered in these deposits, and some regions contain enough $Ca(IO_3)_2$ to serve as a commercial source of iodine.

Volcanic Sublimates

A number of mineral substances are gaseous at the magmatic temperatures of volcanoes and are mobilized with volcanic gases. These kinds of substances condense near the mouths of volcanic fumaroles and are called **sublimates**. Elemental sulfur is a common sublimate. Some oxides, particularly of iron and silicon, are deposited as sublimates. Most other sublimates consist of chloride and sulfate salts. The cations most commonly involved are monovalent cations of ammonium ion, sodium, and potassium; magnesium; calcium; aluminum; and iron. Fluoride and chloride sublimates are sources of gaseous HF and HCl formed by their reactions at high temperatures with water, such as the following:

$$2H_2O + SiF_4 \rightarrow 4HF + SiO_2 \qquad (17.2.1)$$

Igneous, Sedimentary, and Metamorphic Rock

At elevated temperatures deep beneath earth's surface, rocks and mineral matter melt to produce a molten substance called **magma**. Cooling and solidification of magma produces **igneous rock**. Common igneous rocks include granite, basalt, quartz (SiO_2), pyroxene ($(Mg,Fe)SiO_3$), feldspar ($(Ca,Na,K)AlSi_3O_8$), olivine ($(Mg,Fe)_2SiO_4$), and magnetite (Fe_3O_4). Igneous rocks are formed under water-deficient, chemically reducing conditions of high temperature and high pressure. Exposed igneous rocks are under wet, oxidizing, low-temperature, and low-pressure conditions. Since such conditions are opposite those conditions under which igneous rocks were formed, they are not in chemical equilibrium with their surroundings when they become exposed. As a result, such rocks disintegrate by a process called **weathering**. Weathering tends to be slow because igneous rocks are often hard, nonporous, and of low reactivity. Erosion from wind, water, or glaciers picks up materials from weathering rocks and deposits it as **sediments** or **soil**. A process called **lithification** describes the conversion of sediments to **sedimentary rocks**. In contrast to the parent igneous rocks, sediments and sedimentary rocks are porous, soft, and chemically reactive. Heat and pressure convert sedimentary rock to **metamorphic rock**.

Sedimentary rocks may be **detrital rocks** consisting of solid particles eroded from igneous rocks as a consequence of weathering; quartz is the most likely to survive weathering and transport from its original location chemically intact. A second kind of sedimentary rocks consists of **chemical sedimentary rocks** produced by the precipitation or coagulation of dissolved or colloidal weathering products. **Organic sedimentary rocks** contain residues of plant and animal remains. Carbonate minerals of calcium and magnesium—**limestone** or **dolomite**—are especially abundant in sedimentary rocks. Important examples of sedimentary rocks are the following:

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- Sandstone produced from sand-sized particles of minerals such as quartz
- Conglomerates made up of relatively larger particles of variable size
- Shale formed from very fine particles of silt or clay
- Limestone, $CaCO_3$, produced by the chemical or biochemical precipitation of calcium carbonate:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s)$$

$$Ca^{2+} + 2HCO_3^- + h\nu(\text{algal photosynthesis}) \rightarrow \{CH_2O\}(\text{biomass}) + CaCO_3(s) + O_2(g)$$

- Chert consisting of microcrystalline SiO_2

Rock Cycle

The interchanges and conversions among igneous, sedimentary, and metamorphic rocks, as well as the processes involved therein, are described by the **rock cycle**. A rock of any of these three types can be changed to a rock of any other type. Or a rock of any of these three kinds can be changed to a different rock of the same general type in the rock cycle. The rock cycle is illustrated in Figure 17.1.

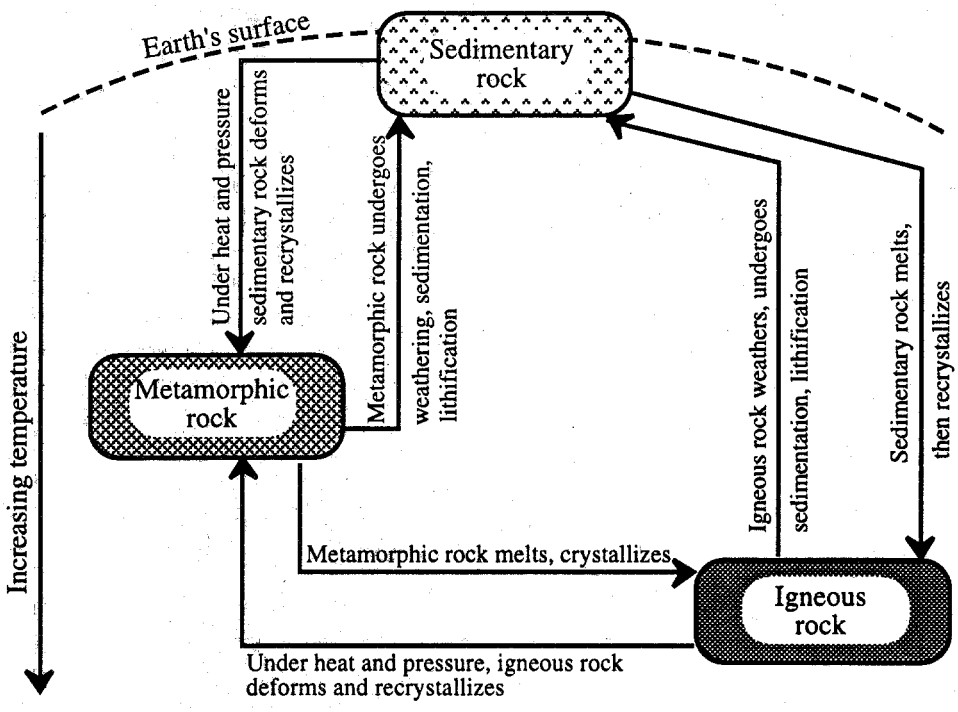


Figure 17.1 The rock cycle

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Stages of Weathering

Weathering can be classified into **early**, **intermediate**, and **advanced stages**. The stage of weathering to which a mineral is exposed depends upon time; chemical conditions, including exposure to air, carbon dioxide, and water; and physical conditions such as temperature and mixing with water and air.

Reactive and soluble minerals such as carbonates, gypsum, olivine, feldspars, and iron(II)-rich substances can survive only early weathering. This stage is characterized by dry conditions, low leaching, absence of organic matter, reducing conditions, and limited time of exposure. Quartz, vermiculite, and smectites can survive the intermediate stage of weathering manifested by retention of silica, sodium, potassium, magnesium, calcium, and iron(II) not present in iron(II) oxides. These substances are mobilized in advanced-stage weathering, other characteristics of which are intense leaching by fresh water, low pH, oxidizing conditions (iron(II) → iron(III)), presence of hydroxy polymers of aluminum, and dispersion of silica.

17.3 PHYSICAL FORM OF THE GEOSPHERE

The most fundamental aspect of the physical form of the geosphere has to do with Earth's shape and dimensions. The earth is shaped as a **geoid** defined by a surface corresponding to the average sea level of the oceans and continuing as hypothetical sea levels under the continents. This shape is not a perfect sphere because of variations in the attraction of gravity at various places on Earth's surface. This slight irregularity in shape is important in surveying to precisely determine the locations of points on Earth's surface according to longitude, latitude, and elevation above sea level. Of more direct concern to humans is the nature of landforms and the processes that occur on them. This area of study is classified as **geomorphology**.

Plate Tectonics and Continental Drift

The geosphere has a highly varied, constantly changing physical form. Most of the earth's land mass is contained in several massive continents separated by vast oceans. Towering mountain ranges spread across the continents, and in some places the ocean bottom is at extreme depths. Earthquakes, which often cause great destruction and loss of life, and volcanic eruptions, which sometimes throw enough material into the atmosphere to cause temporary changes in climate, serve as reminders that the earth is a dynamic, living body that continues to change. There is convincing evidence, such as the close fit between the western coast of Africa and the eastern coast of South America, that widely separated continents were once joined and have moved relative to each other. This ongoing phenomenon is known as **continental drift**. It is now believed that 200 million years ago much of Earth's land mass was all part of a supercontinent, now called Gowandaland. This continent split apart to form the present-day continents of Antarctica, Australia, Africa, and South America, as well as Madagascar, the Seychelle Islands, and India.

The observations described above are explained by the theory of **plate tectonics**. This theory views Earth's solid surface as consisting of several rigid plates that move relative to each other. These plates drift at an average rate of several centimeters per year atop a relatively weak, partially molten layer that is part of

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Earth's upper mantle, called the **asthenosphere**. The science of plate tectonics explains the large-scale phenomena that affect the geosphere, including the creation and enlargement of oceans as the ocean floors open up and spread, the collision and breaking apart of continents, the formation of mountain chains, volcanic activities, the creation of islands of volcanic origin, and earthquakes.

The boundaries between these plates are where most geological activity such as earthquakes and volcanic activity occur. These boundaries are of the three following types:

- **Divergent boundaries** where the plates are moving away from each other. Occurring on ocean floors, these are regions in which hot magma flows upward and cools to produce new solid lithosphere. This new solid material creates **ocean ridges**.
- **Convergent boundaries** where plates move toward each other. One plate may be pushed beneath the other in a **subduction zone** in which matter is buried in the asthenosphere and eventually remelted to form new magma. When this does not occur, the lithosphere is pushed up to form mountain ranges along a collision boundary.
- **Transform fault boundaries** in which two plates slide past each other. These boundaries create faults that result in earthquakes.

The phenomena described above are parts of the **tectonic cycle**, a geological cycle that describes how tectonic plates move relative to each other, magma rises to form new solid rocks, and solid lithospheric rocks sink to become melted, thus forming new magma. The tectonic cycle is illustrated in Figure 17.2.

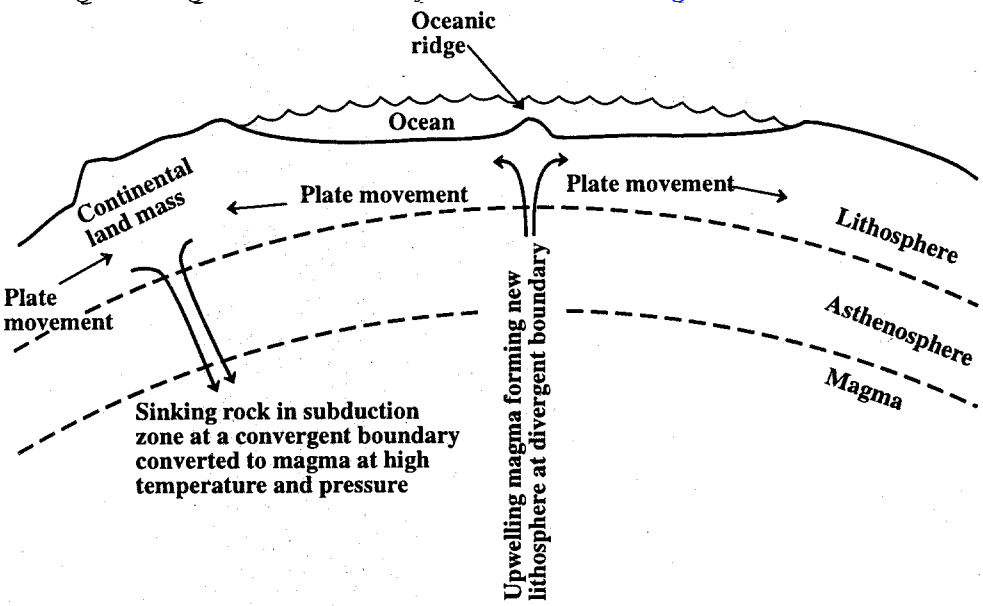


Figure 17.2 Illustration of the techtonic cycle in which upwelling magma along a boundary where two plates diverge creates new lithosphere on the ocean floor, and sinking rock in a subduction zone is melted to form magma.

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Structural Geology

Earth's surface is constantly being reshaped by geological processes. The movement of rock masses during processes such as the formation of mountains results in substantial deformation of rock. At the opposite extreme of the size scale are defects in crystals at a microscopic level. **Structural geology** addresses the geometric forms of geologic structures over a wide range of size, the nature of structures formed by geological processes, and the formation of folds, faults, and other geological structures.

Primary structures are those that have resulted from the formation of a rock mass from its parent materials. Primary structures are modified and deformed to produce **secondary structures.** A basic premise of structural geology is that most layered rock formations were deposited in a horizontal configuration. Cracking of such a formation without displacement of the separate parts of the formation relative to each other produces a **joint**, whereas displacement produces a **fault** (see Figure 17.3).

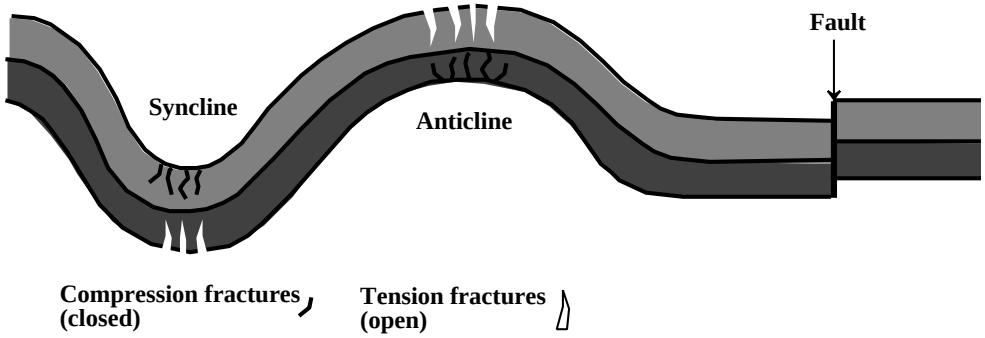


Figure 17.3 Folds (syncline and anticline) are formed by the bending of rock formations. Faults are produced by rock formations moving vertically or laterally in respect to each other.

An important relationship in structural geology is that between the force or **stress** placed upon a geological formation or object and the deformation resulting therefrom, called the **strain**. An important aspect of structural geology, therefore, is **rheology**, which deals with the deformation and flow of solids and semisolids. Whereas rocks tend to be strong, rigid, and brittle under the conditions at Earth's surface, their rheology changes such that they may become weak and pliable under the extreme conditions of temperature and pressure at significant depths below Earth's surface.

Internal and Surface Processes

Related to the physical configuration of the geosphere are several major kinds of processes that occur that change this configuration and that have the potential to cause damage and even catastrophic effects. These can be divided into the two main categories of **internal processes** that arise from phenomena located significantly below the earth's surface, and **surface processes** that occur on the surface.

The two major kinds of internal processes are earthquakes and volcanoes. Earthquakes occur when huge masses of rock formerly locked together abruptly slip relative to each other along a fault. As a result of the movement, the ground may

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shake violently and tremendous damage and loss of life can result. The harmful effects of earthquakes are discussed in some detail in Section 17.9.

Volcanoes are the result of emissions of molten rock (lava), gases, steam, ash, and particles due to the presence of magma near the earth's surface. Like earthquakes, volcanoes are capable of great environmental damage. Environmental aspects of volcanic activity are discussed in Section 17.10.

Geological surface processes occur when rock, soil, mud, ice, or snow move on Earth's surface. Landslides and mudslides, which are discussed in greater detail in Section 17.11, are capable of causing enormous damage and loss of human life. Snow avalanches take a number of lives each winter.

17.4 SEDIMENTS

Vast areas of land, as well as lake and stream sediments, are formed from sedimentary rocks. The properties of these masses of material depend strongly upon their origins and transport. Water is the main vehicle of sediment transport, although wind can also be significant. Hundreds of millions of tons of sediment are carried by major rivers each year.

The action of flowing water in streams cuts away stream banks and carries sedimentary materials for great distances. Sedimentary materials may be carried by flowing water in streams as the following:

- **Dissolved load** from sediment-forming minerals in solution
- **Suspended load** from solid sedimentary materials carried along in suspension
- **Bed load** dragged along the bottom of the stream channel.

The transport of calcium carbonate as dissolved calcium bicarbonate provides a straightforward example of dissolved load and is the most prevalent type of such load. Water with a high dissolved carbon dioxide content (usually present as the result of bacterial action) in contact with calcium carbonate formations contains Ca^{2+} and HCO_3^- ions. Flowing water containing calcium as such *temporary hardness* may become more basic by loss of CO_2 to the atmosphere, consumption of CO_2 by algal growth, or contact with dissolved base, resulting in the deposition of insoluble $CaCO_3$:

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3(s) + CO_2(g) + H_2O \qquad (17.4.1)$$

Most flowing water that contains dissolved load originates underground, where the water has had the opportunity to dissolve minerals from the rock strata that it has passed through.

Most sediments are transported by streams as suspended load, obvious in the observation of "mud" in the flowing water of rivers draining agricultural areas or finely divided rock in Alpine streams fed by melting glaciers. Under normal conditions, finely divided silt, clay, or sand make up most of the suspended load, although larger particles are transported in rapidly flowing water. The degree and

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rate of movement of suspended sedimentary material in streams are functions of the velocity of water flow and the settling velocity of the particles in suspension.

Bed load is moved along the bottom of a stream by the action of water "pushing" particles along. Particles carried as bed load do not move continuously. The grinding action of such particles is an important factor in stream erosion.

Typically, about $^2/_3$ of the sediment carried by a stream is transported in suspension, about $^1/_4$ in solution, and the remaining small fraction as bed load. The ability of a stream to carry sediment increases with both the overall rate of flow of the water (mass per unit time) and the velocity of the water. Both are higher under flood conditions, so floods are particularly important in the transport of sediments.

Streams mobilize sedimentary materials through **erosion**, **transport** materials along with stream flow, and release them in a solid form during **deposition**. Deposits of stream-borne sediments are called **alluvium**. As conditions such as lowered stream velocity begin to favor deposition, larger, more settleable particles are released first. This results in **sorting** such that particles of a similar size and type tend to occur together in alluvial deposits. Much sediment is deposited in flood plains where streams overflow their banks.

17.5 CLAYS

Clays are extremely common and important in mineralogy. Furthermore, in general (see Chapter 18), clays predominate in the inorganic components of most soils and are very important in holding water and in plant nutrient cation exchange. All clays contain silicate and most contain aluminum and water. Physically, clays consist of very fine grains having sheet-like structures. For purposes of discussion here, **clay** is defined as a group of microcrystalline secondary minerals consisting of hydrous aluminum silicates that have sheet-like structures. Clay minerals are distinguished from each other by general chemical formula, structure, and chemical and physical properties. The three major groups of clay minerals are the following:

- **Montmorillonite**, $Al_2(OH)_2Si_4O_{10}$
- **Illite**, $K_{0\text{-}2}Al_4(Si_{8\text{-}6}Al_{0\text{-}2})O_{20}(OH)_4$
- **Kaolinite**, $Al_2Si_2O_5(OH)_4$

Many clays contain large amounts of sodium, potassium, magnesium, calcium, and iron, as well as trace quantities of other metals. Clays bind cations such as Ca^{2+}, Mg^{2+}, K^+, Na^+, and NH_4^+, which protects the cations from leaching by water but keeps them available in soil as plant nutrients. Since many clays are readily suspended in water as colloidal particles, they may be leached from soil or carried to lower soil layers.

Olivine, augite, hornblende, and feldspars are all parent minerals that form clays. An example is the formation of kaolinite ($Al_2Si_2O_5(OH)_4$) from potassium feldspar rock ($KAlSi_3O_8$):

$$2KAlSi_3O_8(s) + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4(s) + 2K^+(aq) + 4H_4SiO_4(aq) \quad (17.5.1)$$

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The layered structures of clays (Figure 17.4) consist of sheets of silicon oxide alternating with sheets of aluminum oxide. The silicon oxide sheets are made up of tetrahedra in which each silicon atom is surrounded by four oxygen atoms. Of the four oxygen atoms in each tetrahedron, three are shared with other silicon atoms that are components of other tetrahedra. This sheet is called the **tetrahedral sheet**. The aluminum oxide is contained in an **octahedral sheet**, so named because each aluminum atom is surrounded by 6 oxygen atoms in an octahedral configuration. The structure is such that some of the oxygen atoms are shared between aluminum atoms and some are shared with the tetrahedral sheet.

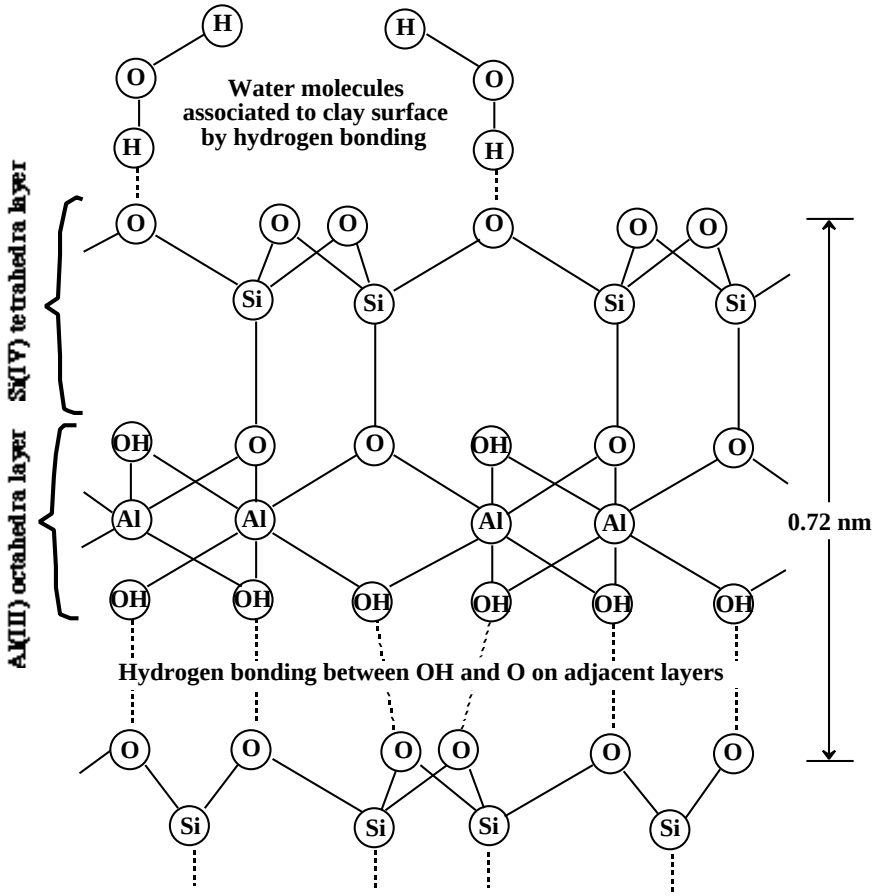


Figure 17.4 Representation of the structure of kaolinite, a two-layer clay.

Structurally, clays can be classified as either **two-layer clays** in which oxygen atoms are shared between a tetrahedral sheet and an adjacent octahedral sheet, and **three-layer clays** in which an octahedral sheet shares oxygen atoms with tetrahedral sheets on either side. These layers composed of either two or three sheets are called **unit layers**. A unit layer of a two-layer clay typically is around 0.7 nanometers (nm) thick, whereas that of a three-layer clay exceeds 0.9 nm in thickness. The structure of the two-layer clay kaolinite is represented in Figure 17.4. Some clays, particularly

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the montmorillonites, may absorb large quantities of water between unit layers, a process accompanied by swelling of the clay.

Clay minerals may attain a net negative charge by **ion replacement**, in which Si(IV) and Al(III) ions are replaced by metal ions of similar size but lesser charge. Compensation must be made for this negative charge by association of cations with the clay layer surfaces. Since these cations need not fit specific sites in the crystalline lattice of the clay, they may be relatively large ions, such as K^+, Na^+, or NH_4^+. These cations are called **exchangeable cations** and are exchangeable for other cations in water. The amount of exchangeable cations, expressed as milliequivalents (of monovalent cations) per 100 g of dry clay, is called the **cation-exchange capacity**, **CEC**, of the clay and is a very important characteristic of colloids and sediments that have cation-exchange capabilities.

17.6 GEOCHEMISTRY

Geochemistry deals with chemical species, reactions, and processes in the lithosphere and their interactions with the atmosphere and hydrosphere. **Environmental geochemistry** is the branch of geochemistry that explores the complex interactions among the rock/water/air/life systems that determine the chemical characteristics of the surface environment. Obviously, geochemistry and its environmental subdiscipline are very important areas of environmental chemistry with many applications related to the environment.

Physical Aspects of Weathering

Defined in Section 17.2, *weathering* is discussed here as a geochemical phenomenon. Rocks tend to weather more rapidly when there are pronounced differences in physical conditions—alternate freezing and thawing and wet periods alternating with severe drying. Other mechanical aspects are swelling and shrinking of minerals with hydration and dehydration, as well as growth of roots through cracks in rocks. Temperature is involved in that the rates of chemical weathering (below) increase with increasing temperature.

Chemical Weathering

As a chemical phenomenon, weathering can be viewed as the result of the tendency of the rock/water/mineral system to attain equilibrium. This occurs through the usual chemical mechanisms of dissolution/precipitation, acid-base reactions, complexation, hydrolysis, and oxidation-reduction.

Weathering occurs extremely slowly in dry air but is many orders of magnitude faster in the presence of water. Water, itself, is a chemically active weathering substance and it holds weathering agents in solution such that they are transported to chemically active sites on rock minerals and contact the mineral surfaces at the molecular and ionic level. Prominent among such weathering agents are CO_2, O_2, organic acids (including humic and fulvic acids, see Section 11.9), sulfur acids ($SO_2(aq)$, H_2SO_4), and nitrogen acids (HNO_3, HNO_2). Water provides the source of H^+ ion needed for acid-forming gases to act as acids as shown by the following:

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$$CO_2 + H_2O \rightarrow H^+ + HCO_3^- \quad (17.6.1)$$

$$SO_2 + H_2O \rightarrow H^+ + HSO_3^- \quad (17.6.2)$$

Rainwater is essentially free of mineral solutes. It is usually slightly acidic due to the presence of dissolved carbon dioxide or more highly acidic because of acid-rain-forming constitutents. As a result of its slight acidity and lack of alkalinity and dissolved calcium salts, rainwater is *chemically aggressive* (see Section 13.7) toward some kinds of mineral matter, which it breaks down by chemical weathering processes. Because of this process, river water has a higher concentration of dissolved inorganic solids than does rainwater.

The processes involved in chemical weathering may be divided into the following major categories:

- **Hydration/dehydration**, for example:

$$CaSO_4(s) + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$$

$$2Fe(OH)_3 \cdot xH_2O(s) \rightarrow Fe_2O_3(s) + (3 + 2x)H_2O$$

- **Dissolution**, for example:

$$CaSO_4 \cdot 2H_2O(s)\ (\text{water}) \rightarrow Ca^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O$$

- **Oxidation**, such as occurs in the dissolution of pyrite:

$$4FeS_2(s) + 15O_2(g) + (8 + 2x)H_2O \rightarrow 2Fe_2O_3 \cdot xH_2O + 8SO_4^{2-}(aq) + 16H^+(aq)$$

or in the following example in which dissolution of an iron(II) mineral is followed by oxidation of iron(II) to iron(III):

$$Fe_2SiO_4(s) + 4CO_2(aq) + 4H_2O \rightarrow 2Fe^{2+} + 4HCO_3^- + H_4SiO_4$$

$$4Fe^{2+} + 8HCO_3^- + O_2(g) \rightarrow 2Fe_2O_3(s) + 8CO_2 + 4H_2O$$

The second of these two reactions may occur at some distance from the first, resulting in net transport of iron from its original location. Iron, manganese, and sulfur are the major elements that undergo oxidation as part of the weathering process.

- **Dissolution with hydrolysis** occurs with the hydrolysis of carbonate ion when mineral carbonates dissolve:

$$CaCO_3(s) + H_2O \rightarrow Ca^{2+}(aq) + HCO_3^-(aq) + OH^-(aq)$$

Hydrolysis is the major means by which silicates undergo weathering as shown by the following reaction of forsterite:

$$Mg_2SiO_4(s) + 4CO_2 + 4H_2O \rightarrow 2Mg^{2+} + 4HCO_3^- + H_4SiO_4$$

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The weathering of silicates yields soluble silicon as species such as H_4SiO_4, and residual silicon-containing minerals (clay minerals).

- **Acid hydrolysis**, which accounts for the dissolution of significant amounts of $CaCO_3$ and $CaCO_3 \cdot MgCO_3$ in the presence CO_2-rich water:

$$CaCO_3(s) + H_2O + CO_2(aq) \rightarrow Ca^{2+}(aq) + 2HCO_3^-(aq)$$

- **Complexation**, as exemplified by the reaction of oxalate ion, $C_2O_4^{2-}$ with aluminum in muscovite, $K_2(Si_6Al_2)Al_4O_{20}(OH)_4$:

$$K_2(Si_6Al_2)Al_4O_{20}(OH)_4(s) + 6C_2O_4^{2-}(aq) + 20\ H^+ \rightarrow 6AlC_2O_4^+(aq) + 6Si(OH)_4 + 2K^+$$

Reactions such as these largely determine the kinds and concentrations of solutes in surface water and groundwater. Acid hydrolysis, especially, is the predominant process that releases elements such as Na^+, K^+, and Ca^{2+} from silicate minerals.

17.7 GROUNDWATER IN THE GEOSPHERE

Groundwater (Figure 17.5) is a vital resource in its own right that plays a crucial role in geochemical processes, such as the formation of secondary minerals. The nature, quality, and mobility of groundwater are all strongly dependent upon the rock formations in which the water is held. Physically, an important characteristic of such formations is their **porosity**, which determines the percentage of rock volume available to contain water. A second important physical characteristic is **permeability**, which describes the ease of flow of the water through the rock. High permeability is usually associated with high porosity. However, clays tend to have low permeability even when a large percentage of the volume is filled with water.

Most groundwater originates as **meteoric** water from precipitation in the form of rain or snow. If water from this source is not lost by evaporation, transpiration, or to stream runoff, it may infiltrate into the ground. Initial amounts of water from precipitation onto dry soil are held very tightly as a film on the surfaces and in the micropores of soil particles in a **belt of soil moisture**. At intermediate levels, the soil particles are covered with films of water, but air is still present in larger voids in the soil. The region in which such water is held is called the **unsaturated zone** or **zone of aeration** and the water present in it is **vadose water**. At lower depths in the presence of adequate amounts of water, all voids are filled to produce a **zone of saturation**, the upper level of which is the **water table**. Water present in a zone of saturation is called **groundwater**. Because of its surface tension, water is drawn somewhat above the water table by capillary-sized passages in soil in a region called the capillary fringe.

The water table (Figure 17.6) is crucial in explaining and predicting the flow of wells and springs and the levels of streams and lakes. It is also an important factor in determining the extent to which pollutant and hazardous chemicals underground are

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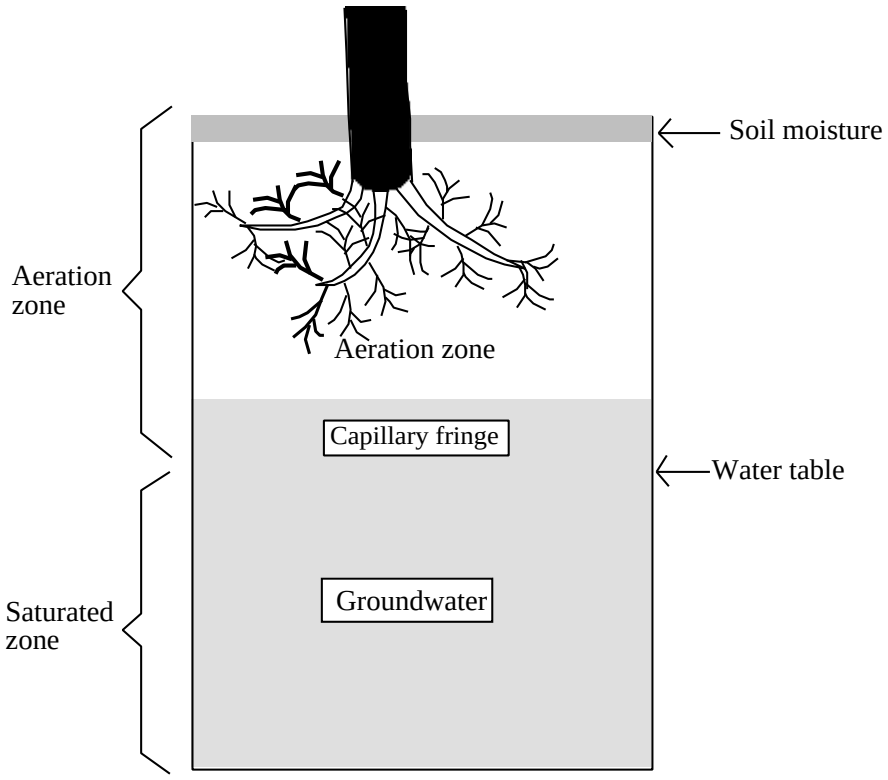


Figure 17.5 Some major features of the distribution of water underground.

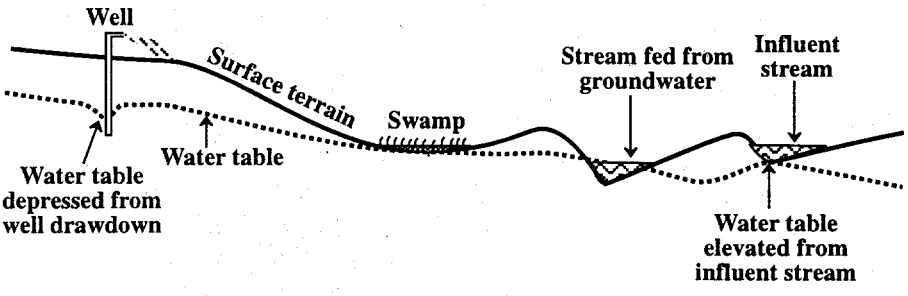


Figure 17.6 The water table and influences of surface features on it.

likely to be transported by water. The water table can be mapped by observing the equilibrium level of water in wells, which is essentially the same as the top of the saturated zone. The water table is usually not level, but tends to follow the general contours of the surface topography. It also varies with differences in permeability and water infiltration. The water table is at surface level in the vicinity of swamps and frequently above the surface where lakes and streams are encountered. The water level in such bodies may be maintained by the water table. **Influent** streams or reservoirs are located above the water table; they lose water to the underlying aquifer and cause an upward bulge in the water table beneath the surface water.

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Groundwater **flow** is an important consideration in determining the accessibility of the water for use and transport of pollutants from underground waste sites. Various parts of a body of groundwater are in hydraulic contact so that a change in pressure at one point will tend to affect the pressure and level at another point. For example, infiltration from a heavy localized rainfall may affect the water table at a point remote from the infiltration. Groundwater flow occurs as the result of the natural tendency of the water table to assume even levels by the action of gravity.

Groundwater flow is strongly influenced by rock permeability. Porous or extensively fractured rock is relatively highly **pervious**, meaning that water can migrate through the holes, fissures, and pores in such rock. Because water can be extracted from such a formation, it is called an **aquifer**. By contrast, an **aquiclude** is a rock formation that is too impermeable or unfractured to yield groundwater. Impervious rock in the unsaturated zone may retain water infiltrating from the surface to produce a **perched water table** that is above the main water table and from which water may be extracted. However, the amounts of water that can be extracted from such a formation are limited and the water is vulnerable to contamination.

Water Wells

Most groundwater is tapped for use by water wells drilled into the saturated zone. The use and misuse of water from this source has a number of environmental implications. In the U.S., about 2/3 of the groundwater pumped is consumed for irrigation; lesser amounts of groundwater are used for industrial and municipal applications.

As water is withdrawn, the water table in the vicinity of the well is lowered. This **drawdown** of water creates a **zone of depression**. In extreme cases the groundwater is severely depleted and surface land levels can even subside (which is one reason that Venice, Italy is now very vulnerable to flooding). Heavy drawdown can result in infiltration of pollutants from sources such as septic tanks, municipal refuse sites, and hazardous-waste dumps. When soluble iron(II) or manganese(II) are present in groundwater, exposure to air at the well wall can result in the formation of deposits of insoluble iron(III) and manganese(IV) oxides produced by bacterially catalyzed processes:

$$4Fe^{2+}(aq) + O_2(aq) + 10H_2O \rightarrow 4Fe(OH)_3(s) + 8H^+ \quad (17.7.1)$$

$$2Mn^{2+}(aq) + O_2(aq) + (2x + 2)H_2O \rightarrow 2MnO_2 \cdot xH_2O(s) + 4H^+ \quad (17.7.2)$$

Deposits of iron(III) and manganese(IV) that result from the processes outlined above line the surfaces from which water flows into the well with a coating that is relatively impermeable to water. The deposits fill the spaces that water must traverse to enter the well. As a result, they can seriously impede the flow of water into the well from the water-bearing aquifer. This creates major water source problems for municipalities using groundwater for water supply. As a result of this problem, chemical or mechanical cleaning, drilling of new wells, or even acquisition of new water sources may be required.

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17.8 ENVIRONMENTAL ASPECTS OF THE GEOSPHERE

Most of the remainder of this chapter deals specifically with the environmental aspects of geology and human interactions with the geosphere. The following sections discuss how natural geological phenomena affect the environment through occurrences such as volcanic eruptions that might blast so much particulate matter and acid gas into the atmosphere that it could have a temporary effect on global climate, or massive earthquakes that disrupt surface topography and disturb the flow and distribution of groundwater and surface water. Also discussed are human influences on the geosphere and the strong connection between the geosphere and the anthrosphere.

Going back several billion years to its formation as a ball of dust particles collected from the universe and held together by gravitational forces, earth has witnessed constant environmental change and disruption. During its earlier eons, earth was a most inhospitable place for humans and, indeed, for any form of life. Heat generated by gravitational compression of primitive earth and by radioactive elements in its interior caused much of the mass of the planet to liquify. Relatively high-density iron sank into the core, and lighter minerals, primarily silicates, solidified and floated to the surface.

Although Earth changes almost imperceptibly during a human lifetime, the planet is in fact in a state of constant change and turmoil. It is known that continents have formed, broken apart, and moved around. Rock formations produced in ancient oceans have been thrust up onto continental land and huge masses of volcanic rock exist where volcanic activity is now unknown and has been absent for millions of years. Earth still unleashes enormous forces that push molten rock to the surface and move continents continuously as evidenced from volcanic activity, and from earthquakes resulting from the movement of great land masses relative to each other. Earth's surface is constantly changing as new mountain ranges are heaved up and old ones are worn down.

Humans have learned to work with, against, and around natural earth processes and phenomena to exploit earth's resources and to make these processes and phenomena work for the benefit of humankind. Human efforts have been moderately successful in mitigating some of the major hazards posed by natural geospheric phenomena, although such endeavors often have had unforeseen detrimental consequences that sometimes are not manifested until many years after they were first applied. The survival of modern civilization and, indeed, of humankind will depend upon how intelligently humans work with the earth, rather than against it. That is why it is so important for humans to have a fundamental understanding of the geospheric environment.

An important consideration in human interaction with the geosphere is the application of engineering to geology. Engineering geology takes account of the geological characteristics of soil and rock in designing buildings, dams, highways, and other structures in a manner compatible with the geological strata on which they rest. Engineering geology must consider a large number of geological factors including type, strength, and fracture characteristics of rock, tendency for landslides to occur, susceptibility to settling, and likelihood of erosion. Engineering geology is an important consideration in land-use planning.

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Natural Hazards

Earth presents a variety of natural hazards to the creatures that dwell on it. Some of these are the result of internal processes that arise from the movement of land masses relative to each other and from heat and intrusions of molten rock from below the surface. The most common such hazards are earthquakes and volcanoes. Whereas internal processes tend to force matter upward, often with detrimental effects, surface processes are those that generally result from the tendency of matter to seek lower levels. Such processes include erosion, landslides, avalanches, mud-flows, and subsidence.

A number of natural hazards result from the interaction and conflict between solid Earth and liquid and solid water. Perhaps the most obvious such hazard consists of floods when too much water falls as precipitation and seeks lower levels through streamflow. Wind can team with water to increase destructive effects, such as beach erosion and destruction of beachfront property resulting from wind-driven seawater. Ice, too, can have some major effects on solid earth. Evidence of such effects from Ice Age times include massive glacial moraines left over from deposition of till from melting glaciers, and landscape features carved by advancing ice sheets.

Anthropogenic Hazards

All too often, attempts to control and reshape the geosphere to human demands have been detrimental to the geosphere and dangerous to human life and well-being. Such attempts may exacerbate damaging natural phenomena. A prime example of this interaction occurs when efforts are made to control the flow of rivers by straightening them and building levees. The initial results can be deceptively favorable in that a modified stream may exist for decades, flowing smoothly and staying within the confines imposed by humans. But eventually, the forces of nature are likely to overwhelm the efforts of humans to control them, such as when a record flood breaks levees and destroys structures constructed in flood-prone areas. Landslides of mounds of earthen material piled up from mining can be very destructive. Destruction of wetlands in an effort to provide additional farmland can have some detrimental effects upon wildlife and upon the overall health of ecosystems.

17.9 EARTHQUAKES

Earthquakes usually arise from plate tectonic processes and originate along plate boundaries occurring as motion of ground resulting from the release of energy that accompanies an abrupt slippage of rock formations subjected to stress along a fault. Basically, two huge masses of rock tend to move relative to each other, but are locked together along a fault line. This causes deformation of the rock formations, which increases with increasing stress. Eventually, the friction between the two moving bodies is insufficient to keep them locked in place, and movement occurs along an existing fault, or a new fault is formed. Freed from constraints on their movement, the rocks undergo elastic rebound, causing the earth to shake, often with catastrophic effects.

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The location of the initial movement along a fault that causes an earthquake to occur is called the **focus** of the earthquake. The surface location directly above the focus is the **epicenter**. Energy is transmitted from the focus by **seismic waves**. Seismic waves that travel through the interior of the earth are called **body waves** and those that traverse the surface are **surface waves**. Body waves are further categorized as **P-waves**, compressional vibrations that result from the alternate compression and expansion of geospheric material, and **S-waves**, consisting of shear waves manifested by sideways oscillations of material. The motions of these waves are detected by a **seismograph**, often at great distances from the epicenter. The two types of waves move at different rates, with P-waves moving faster. From the arrival times of the two kinds of waves at different seismographic locations, it is possible to locate the epicenter of an earthquake.

Adding to the terror of earthquakes is their lack of predictability. An earthquake can strike at any time—during the calm of late night hours or in the middle of busy rush hour traffic. Although the exact prediction of earthquakes has so far eluded investigators, the locations where earthquakes are most likely to occur are much better known. These are located in lines corresponding to boundaries along which tectonic plates collide and move relative to each other, building up stresses that are suddenly released when earthquakes occur. Such interplate boundaries are locations of preexisting faults and breaks. Occasionally, however, an earthquake will occur within a plate, made more massive and destructive because when it occurs the thick lithosphere is ruptured.

The scale of earthquakes can be estimated by the degree of motion that they cause and by their destructiveness. The former is termed the **magnitude** of an earthquake and is commonly expressed by the **Richter scale**. The Richter scale is open-ended, and each unit increase in the scale reflects a 10-fold increase in magnitude. Several hundred thousand earthquakes with magnitudes from 2 to 3 occur each year; they are detected by seismographs, but are not felt by humans. Minor earthquakes range from 4 to 5 on the Richter scale, and earthquakes cause damage at a magnitude greater than about 5. Great earthquakes, which occur about once or twice a year, register over 8 on the Richter scale.

The **intensity** of an earthquake is a subjective estimate of its potential destructive effect. On the Mercalli intensity scale, an intensity III earthquake feels like the passage of heavy vehicles; one with an intensity of VII causes difficulty in standing, damage to plaster, and dislodging of loose brick, whereas a quake with an intensity of XII causes virtually total destruction, throws objects upward, and shifts huge masses of earthen material. Intensity does not correlate exactly with magnitude.

Distance from the epicenter, the nature of underlying strata, and the types of structures affected may all result in variations in intensity from the same earthquake. In general, structures built on bedrock will survive with much less damage than those constructed on poorly consolidated material. Displacement of ground along a fault can be substantial, for example, up to 6 or 7 meters along the San Andreas fault during the 1906 San Francisco earthquake. Such shifts can break pipelines and destroy roadways. Highly destructive surface waves can shake vulnerable structures apart.

The shaking and movement of ground are the most obvious means by which earthquakes cause damage. In addition to shaking the ground, earthquakes can cause

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it to rupture, subside, or rise. **Liquefaction** is an important phenomenon that occurs during earthquakes with ground that is poorly consolidated and in which the water table may be high. Liquefaction results from separation of soil particles accompanied by water infiltration such that the ground behaves like a fluid.

Another devastating phenomenon consists of **tsunamis**, large ocean waves resulting from earthquake-induced movement of the ocean floor. Tsunamis sweeping onshore at speeds up to 1000 km/hr have destroyed many homes and taken many lives, often large distances from the epicenter of the earthquake itself. This effect occurs when a tsunami approaches land and forms huge breakers, some as high as 10–15 meters, or even higher. On April 1, 1946, an earthquake off the coast of Alaska generated a Tsunami estimated to be more than 30 meters high that killed 5 people in a nearby lighthouse. About 5 hours later, a Tsunami generated by the same earthquake reached Hilo, Hawaii, and killed 159 people with a wave exceeding 15 meters high. The March 27, 1964, Alaska earthquake generated a tsunami over 10 meters high that hit a freighter docked at Valdez, tossing it around like matchwood. Miraculously, nobody on the freighter was killed, but 28 people on the dock died.

Literally millions of lives have been lost in past earthquakes, and damage from an earthquake in a developed urban area can easily run into billions of dollars. As examples, a massive earthquake in Egypt and Syria in 1201 A.D. took over 1 million lives, one in Tangshan, China, in 1976 killed about 650,000, and the 1989 Loma Prieta earthquake in California cost about 7 billion dollars. Numerous lives were lost in earthquakes that took place in Turkey, Greece, and Taiwan in 1999.

Significant progress has been made in designing structures that are earthquake-resistant. As evidence of that, during a 1964 earthquake in Niigata, Japan, some buildings tipped over on their sides due to liquefaction of the underlying soil, but remained structurally intact! Other areas of endeavor that can lessen the impact of earthquakes is the identification of areas susceptible to earthquakes, discouraging development in such areas, and educating the public about earthquake hazards. Accurate prediction would be a tremendous help in lessening the effects of earthquakes, but so far has been generally unsuccessful. Most challenging of all is the possibility of preventing major earthquakes. One unlikely possibility would be to detonate nuclear explosives deep underground along a fault line to release stress before it builds up to an excessive level. Fluid injection to facilitate slippage along a fault has also been considered.

17.10 VOLCANOES

Volcanoes

In addition to earthquakes, the other major subsurface process that has the potential to massively affect the environment consists of emissions of molten rock (lava), gases, steam, ash, and particles due to the presence of magma near the earth's surface. This phenomenon is called a **volcano** (Figure 17.7). Volcanoes can be very destructive and damaging to the environment.

Volcanoes take on a variety of forms that are beyond the scope of this chapter to cover in detail. Basically, they are formed when magma rises to the surface. This frequently occurs in subduction zones created where one plate is pushed beneath

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another (see Figure 17.2). The downward movement of solid lithospheric material subjects it to high temperatures and pressures that cause the rock in it to melt and rise to the surface as magma. Molten magma issuing from a volcano at temperatures usually in excess of 500˚C, and often as high as 1,400˚C, is called **lava**, and is one of the more common manifestations of volcanic activity.

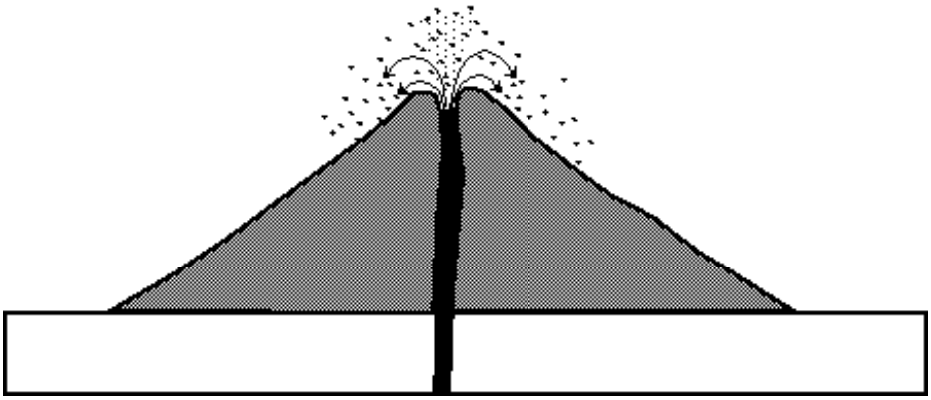


Figure 17.7 Volcanoes come in many shapes and forms. A classically shaped volcano may be a cinder cone formed by ejection of rock and lava, called pyroclastics, from the volcano to produce a relatively uniform cone.

On May 18, 1980, Mount St. Helens, a volcano in Washington State, erupted, blowing out about 1 cubic kilometer of material. This massive blast spread ash over half the United States, causing about $1 billion in damages and killing an estimated 62 people, many of whom were never found. Many volcanic disasters have been recorded throughout history. Perhaps the best known of these is the 79 A.D. eruption of Mount Vesuvius, which buried the Roman city of Pompei with volcanic ash.

Temperatures of **lava**, molten rock flowing from a volcano, typically exceed 500˚C and may get as high as 1400˚C or more. Lava flows destroy everything in their paths, causing buildings and forests to burn and burying them under rock that cools and becomes solid. Often more dangerous than a lava flow are the **pyroclastics** produced by volcanoes and consisting of fragments of rock and lava. Some of these particles are large and potentially very damaging, but they tend to fall quite close to the vent. Ash and dust may be carried for large distances and, in extreme cases, as was the case in ancient Pompei, may bury large areas to some depth with devastating effects. The explosion of Tambora volcano in Indonesia in 1815 blew out about 30 cubic kilometers of solid material. The ejection of so much solid into the atmosphere had such a devastating effect on global climate that the following year was known as “the year without a summer,” causing widespread hardship and hunger because of global crop failures.

A special kind of particularly dangerous pyroclastic consists of **nuée ardente**. This term, French for “glowing cloud,” refers to a dense mixture of hot toxic gases and fine ash particles reaching temperatures of 1000˚C that can flow down the slopes of a volcano at speeds of up to 100 km/hr. In 1902 a nuée ardente was produced by the eruption of Mont Pelée on Martinique in the Caribbean. Of as many as 40,000 people in the town of St. Pierre, the only survivor was a terrified prisoner shielded from the intense heat by the dungeon in which he was imprisoned.

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One of the more spectacular and potentially damaging volcanic phenomena is a **phreatic eruption** which occurs when infiltrating water is superheated by hot magma and causes a volcano to literally explode. This happened in 1883 when uninhabited Krakatoa in Indonesia blew up with an energy release of the order of 100 megatons of TNT. Dust was blown 80 kilometers into the stratosphere, and a perceptible climatic cooling was noted for the next 10 years. As is the case with earthquakes, volcanic eruptions may cause devastating tsunamis. Krakatoa produced a tsunami 40 meters high that killed 30 to 40 thousand people on surrounding islands.

Some of the most damaging health and environmental effects of volcanic eruptions are caused by gases released to the atmosphere. Huge quantities of water vapor are often evolved. Dense carbon dioxide gas can suffocate people near the point of release. Highly toxic H_2S and CO gases may be released by volcanoes. Volcanoes tend to give off acid gases such as hydrogen chloride produced by the subduction and heating of sodium chloride entrained in ocean sediment. Sulfur oxides released by volcanoes may affect the atmosphere. In 1982 El Chichón erupted in Mexico, producing comparatively little dust but huge quantities of sulfur oxides. These gases were converted to sulfuric acid droplets in the atmosphere, which reflected enough sunlight to cause a perceptible cooling in climate. Eventually the sulfuric acid released fell as acidic precipitation, "acid rain."

Volcanic activity could change the global environment dramatically. Massive volcanic eruptions many millions of years ago were probably responsible for widespread extinctions of organisms on earth's surface. These effects occur primarily by the ejection of particles and sulfuric acid precursors into the atmosphere causing global cooling and potential harm to the protective stratospheric ozone layer. Although such an extinction event is unlikely in modern times, a volcanic eruption such as that of the Tambora volcano described above could certainly happen. With humankind "living on the edge" as far as grain supplies are concerned, widespread starvation resulting from a year or two of crop failures would almost certainly occur.

17.11 SURFACE EARTH MOVEMENT

Surface geological features are formed by upward movement of materials from earth's crust. With exposure to water, oxygen, freeze-thaw cycles, organisms, and other influences on the surface, surface features are subject to two processes that largely determine the landscape—weathering and erosion. As noted earlier in this chapter, weathering consists of the physical and chemical breakdown of rock, and erosion is the removal and movement of weathered products by the action of wind, liquid water, and ice. Weathering and erosion work together in that one augments the other in breaking down rock and moving the products. Weathered products removed by erosion are eventually deposited as sediments and may undergo diagenesis and lithification to form sedimentary rocks.

One of the most common surface processes that can adversely affect humans consists of **landslides** that occur when soil or other unconsolidated materials slide down a slope. Related phenomena include rockfalls, mudflows, and snow avalanches. As shown in Figure 17.8, a landslide typically consists of an upper slump that is prevented from sliding farther by a mass of material accumulated in a lower

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flow. Figure 17.8 illustrates what commonly happens in a landslide when a mass of earth moves along a slip plane under the influence of gravity. The stability of earthen material on a slope depends upon a balance between the mass of slope material and the resisting force of the shear strength of the slope material. There is a tendency for the earth to move along slip planes. In addition to the earthen material itself, water, vegetation, and structures constructed by humans may increase the driving force leading to a landslide. The shear strength is, of course, a function of the geological material along the slip plane and may be affected by other factors as well, such as the presence of various levels of water and the degree and kinds of vegetation growing on the surface.

The tendency of landslides to form is influenced by a number of outside factors. Climate is important because it influences the accumulation of water that often precedes a landslide as well as the presence of plants that can also influence soil stability. Although it would seem that plant roots should stabilize soil, the ability of some plants to add significant mass to the slope by accumulating water and to destabilize soil by aiding water infiltration may have an opposite effect, making soil on a slope much more susceptible to landslides. Disturbance of earth by road building or other construction may cause landslides to occur. Earth may be shaken loose by earthquakes, causing landslides to occur.

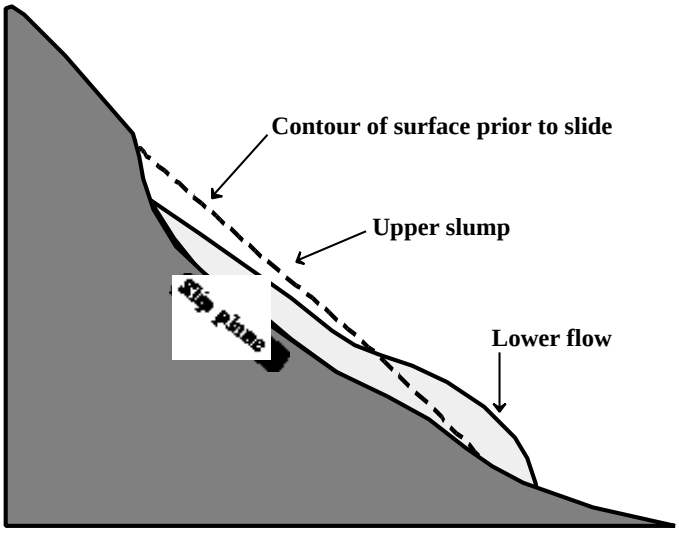


Figure 17.8 A landslide occurs when earth moves along a slip plane. Typically, a landslide consists of an upper slump and lower flow. The latter serves to stabilize the slide, and when it is disturbed, such as by cutting through it to construct a road, the earth may slide farther.

Loss of life and property from landslides can be substantial. In 1970, a devastating avalanche of soil, mud, and rocks initiated by an earthquake slid down Mt. Huascaran in Peru killing an estimated 20,000 people. Sometimes the effects are indirect. In 1963 as many as 2600 people were killed near the Vaiont Dam in Italy. A sudden landslide filled the reservoir behind the dam with earthen material and, although the dam held, the displaced water spilled over its abutments as a wave 90 meters high, wiping out structures and lives in its path.

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Although often ignored by developers, the tendency toward landslides is predictable. Knowledge of the tendency for landslides to occur can be used to determine areas in which homes and other structures should not be built. Slope stability maps based upon the degree of slope, the nature of underlying geological strata, climatic conditions, and other factors can be used to assess the risk of landslides. Evidence of a tendency for land to slide can be observed from effects on existing structures, such as walls that have lost their alignment, cracks in foundations, and poles that tilt. The likelihood of landslides can be minimized by moving material from the upper to the lower part of a slope, avoiding the loading of slopes, and avoiding measures that might change the degree and pathways of water infiltration into slope materials. In cases where the risk is not too severe, retaining walls can be constructed to reduce the effects of landslides.

Several measures can be used to warn of landslides. Simple visual observations of changes in the surface can be indicative of an impending landslide. More sophisticated measures include tilt meters and devices that sense vibrations accompanying the movement of earthen materials.

In addition to landslides, there are several other kinds of mass movements that have the potential to be damaging. **Rockfalls** occur when rocks fall down slopes so steep that at least part of the time the falling material is not in contact with the ground. The fallen material accumulates at the bottom of the fall as a pile of **talus**. A much less spectacular event is **creep**, in which movement is slow and gradual. The action of frost—frost heaving—is a common form of creep. Though usually not life-threatening, over a period of time creep may ruin foundations and cause misalignment of roads and railroads with significant, often very costly, property damage frequently the result.

Special problems are presented by permanently frozen ground in arctic climates such as Alaska or Siberia. In such areas the ground may remain permanently frozen, thawing to only a shallow depth during the summer. This condition is called **permafrost**. Permafrost poses particular problems for construction, particularly where the presence of a structure may result in thawing such that the structure rests in a pool of water-saturated muck resting on a slick surface of frozen water and soil. The construction and maintenance of highways, railroads, and pipelines, such as the Trans-Alaska pipeline in Alaska, can become quite difficult in the presence of permafrost.

Some types of soils, particularly so-called expansive clays, expand and shrink markedly as they become saturated with water and dry out. Although essentially never life-threatening, the movement of structures and the damage caused to them by expansive clays can be very high. Aside from years when catastrophic floods and earthquakes occur, the monetary damage done by the action of expansive soil exceeds that of earthquakes, landslides, floods, and coastal erosion combined.

Sinkholes are a kind of earth movement resulting when surface earth falls into an underground cavity. They rarely injure people but occasionally causes spectacular property damage. Cavities that produce sinkholes may form by the action of water containing dissolved carbon dioxide on limestone (See Chapter 11, Reaction 11.7.6); loss of underground water during drought or from heavy pumping, thus removing support that previously kept soil and rock from collapsing; heavy underground water flow; and other factors that remove solid material from underground strata.

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17.12 STREAM AND RIVER PHENOMENA

A **stream** consists of water flowing through a channel. The area of land from which water that flows into a stream is drawn is the stream's **drainage basin**. The sizes of streams are described by **discharge** defined as the volume of water flowing past a given point on the stream per unit time. Discharge and **gradient**, the steepness of the downward slope of a stream determine the stream **velocity**.

Internal processes raise masses of land and whole mountain ranges, which in turn are shaped by the action of streams. Streams cut down mountain ranges, create valleys, form plains, and produce great deposits of sediment, thus playing a key role in shaping the geospheric environment. Streams spontaneously develop bends and curves by cutting away the outer parts of stream banks and depositing materials on the inner parts. These curved features of streams are known as **meanders**. Left undisturbed, a stream forms meanders across a valley in a constantly changing pattern. The cutting away of material by the stream and the deposition of sediment eventually forms a generally flat area. During times of high stream flow, the stream leaves its banks, inundating parts or all of the valley. The accompanying erosion and deposition of matter creates a **floodplain**.

A **flood** occurs when a stream develops a high flow such that it leaves its banks and spills out onto the floodplain. Floods are arguably the most common and damaging of surface phenomena in the geosphere. Though natural and in many respects beneficial occurrences, floods cause damage to structures located in their paths, and the severity of their effects is greatly increased by human activities.

A number of factors determine the occurrence and severity of floods. One of these is the tendency of particular geographic areas to receive large amounts of rain within short periods of time. One such area is located in the middle of the continental United States, where warm, moisture-laden air from the Gulf of Mexico is carried northward during the spring months to collide with cold air from the north; the resultant cooling of the moist air can cause torrential rains to occur, resulting in severe flooding. In addition to season and geography, geological conditions have a strong effect on flooding potential. Rain falling on a steep surface tends to run off rapidly, creating flooding. A watershed can contain relatively massive quantities of rain if it consists of porous, permeable materials that allow a substantial rate of infiltration, assuming that it is not already saturated. Plants in a watershed tend to slow runoff and loosen soil, enabling additional infiltration. Through transpiration (see Chapter 18, Section 18.2), plants release moisture to the atmosphere quickly, enabling soil to absorb more moisture.

Several terms are used to describe flooding. When the **stage** of a stream, that is, the elevation of the water surface, exceeds the stream bank level, the stream is said to be at **flood stage**. The highest stage attained defines the flood **crest**. **Upstream** floods occur close to the inflow from the drainage basin, usually the result of intense rainfall. Whereas upstream floods usually affect smaller streams and watersheds, **downstream floods** occur on larger rivers that drain large areas. Widespread spring snowmelt and heavy, prolonged spring rains, often occurring together, cause downstream floods.

Floods are made more intense by higher fractions and higher rates of runoff,

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both of which may be aggravated by human activities. This can be understood by comparing a vegetated drainage basin to one that has been largely denuded of vegetation and paved over. In the former case, rainfall is retained by vegetation, such as grass cover. Thus, the potential flood water is delayed, the time span over which it enters a stream is extended, and a higher proportion of the water infiltrates into the ground. In the latter case, less rainfall infiltrates, and the runoff tends to reach the stream quickly and to be discharged over a shorter time period, thus leading to more-severe flooding. These factors are illustrated in Figure 17.9.

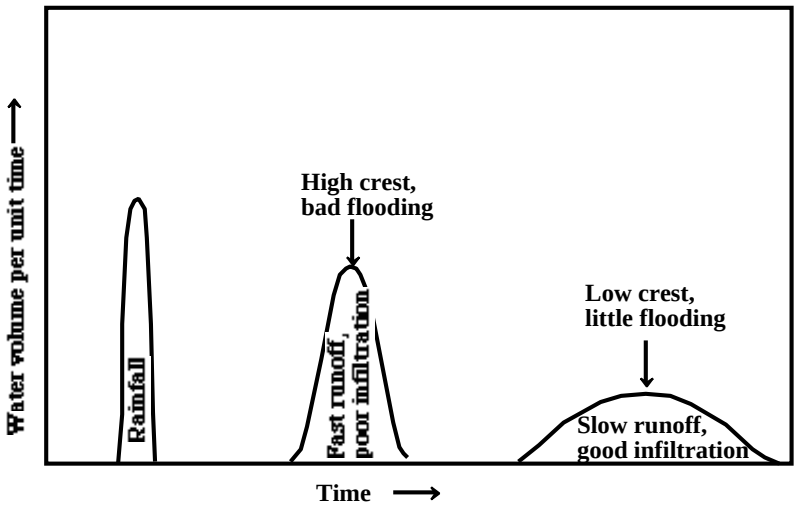


Figure 17.9 Influence of runoff on flooding.

The conventional response to the threat of flooding is to control a river, particularly by the construction of raised banks called **levees**. In addition to raising the banks to contain a stream, the stream channel may be straightened and deepened to increase the volume and velocity of water flow, a process called **channelization**. Although effective for common floods, these measures may exacerbate extreme floods by confining and increasing the flow of water upstream such that the capacity to handle water downstream is overwhelmed. Another solution is to construct dams to create reservoirs for flood control upstream. Usually, such reservoirs are multipurpose facilities designed for water supply, recreation, and to control river flow for navigation in addition to flood control. The many reservoirs constructed for flood control in recent decades have been reasonably successful. There are, however, conflicts in the goals for their uses. Ideally, a reservoir for flood control should remain largely empty until needed to contain a large volume of floodwater, an approach that is obviously inconsistent with other uses. Another concern is that of exceeding the capacity of the reservoir, or dam failure, the latter of which can lead to catastrophic flooding.

17.13 PHENOMENA AT THE LAND–OCEAN INTERFACE

The coastal interface between land masses and the ocean is an important area of environmental activity. The land along this boundary is under constant attack from

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the waves and currents from the ocean, so that most coastal areas are always changing. The most common structure of the coast is shown in cross section in Figure 17.10. The beach, consisting of sediment, such as sand formed by wave action on coastal rock, is a sloping area that is periodically inundated by ocean waves. Extending from approximately the high tide mark to the dunes lining the landward edge of the beach is a relatively level area called the **berm**, which is usually not washed over by ocean water. The level of water to which the beach is subjected varies with the tides. Through wind action, the surface of the water is in constant motion as undulations called **ocean waves**. As these waves reach the shallow water along the beach, they "touch bottom" and are transformed to **breakers**, characterized by crested tops. These breakers crashing onto a beach give it much of its charm, but can also be extremely destructive.

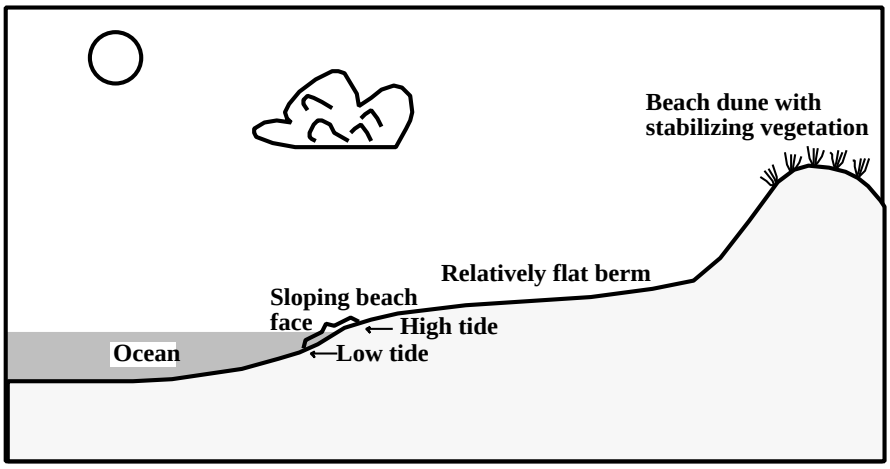


Figure 17.10 Cross section of the ocean/land interface along a beach.

Coastlines exhibit a variety of features. Steep valleys carved by glacial activity, then filled with rising seawater, constitute the picturesque fjords characteristic of much of the coast of Norway. Valleys, formerly on land, now filled with seawater, constitute **drowned valleys**. **Estuaries** occur where tidal salt water mixes with inflowing fresh water.

Erosion is a constant feature of a beachfront. Unconsolidated beach sand can be shifted readily, sometimes spectacularly through great distances over short periods of time, by wave action. Sand, pebbles, and rock in the form of rounded cobbles constantly wear against the coast by wave action, exerting a constant abrasive action called **milling**. This action is augmented by the chemical weathering effects of seawater, in which the salt content may play a role.

Some of the more striking alterations to coastlines occur during storms such as hurricanes and typhoons. The low pressure that accompanies severe storms tends to suck ocean water upward. This effect, usually combined with strong winds blowing onshore and coinciding with high tide, can cause ocean water to wash over the berm on a beach to attack dunes or cliffs inland. Such a **storm surge** can remove large quantities of beach, damage dune areas, and wash away structures unwisely constructed too close to the shore. A storm surge associated with a hurricane washed

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away most of the structures in Galveston, Texas, in 1900, claiming 6000 lives.

An especially vulnerable part of the coast consists of barrier islands, long, low strips of land roughly paralleling the coast some distance offshore. High storm surges may wash completely over barrier islands, partially destroying them and shifting them around. Many dwellings unwisely constructed on barrier islands, such as the outer banks of North Carolina, have been destroyed by storm surges during hurricanes.

The Threat of Rising Sea Levels

Any significant temporary or permanent rise in sea level poses significant risks to lives and property of large numbers of people who live at, or in some cases even below, sea level. Such an event occurred on February 1, 1953, in the Netherlands. This event occurred when high tides and strong winds combined to breach the system of dikes protecting much of the Netherlands from seawater. About 1/6 of the country was flooded as far inland as 64 kilometers from the coast. A total of approximately 2000 people were killed by the severe flooding and approximately 100,000 people were left without homes.

Although isolated instances of flooding by seawater caused by combinations of tidal and weather phenomena will continue to occur, a much more long-lasting threat, and one not nearly so amenable to remediation measures, such as dike construction, is posed by long-term increases in sea level. These could result from global warming due to the greenhouse gas emissions discussed in Chapter 15. Several phenomena associated with global warming have the potential to raise ocean levels to destructive highs. Simple expansion of warmed oceanic water could raise sea levels by about 1/3 meter over the next century. The melting of glaciers, such as those in the Alps, has probably raised ocean levels about 5 cm during the last century, and the process is continuing. The greatest concern, however, is that global warming could cause the great West Antarctic ice sheet to melt, which would raise sea levels by as much as 6 meters.

Much uncertainty exists regarding the possibility of the West Antarctic ice sheet's melting and causing increases in sea level. There should be some compensating effect in that hotter air produced by greenhouse warming could carry much more atmospheric moisture to the Antarctic regions where the moisture would be deposited as snow. The net result could well be an *increase* in solid snow and ice in the Antarctic, and an accompanying *decrease* in sea levels. Some of the uncertainty regarding the status of the West Antarctic ice sheet may be alleviated in the future by highly accurate space satellite measurements. The measurement of sea levels has proven to be a difficult task because the levels of the surface of land keep changing. Land most recently covered with Ice Age glaciers in areas such as Scandinavia is still "springing back" from the immense mass of the glaciers, so that sea levels measured by gauges fixed on land actually appear to be dropping by several millimeters per year in such locations. An opposite situation exists on the east coast of North America, where land was pushed outward and raised around the edge of the enormous sheet of ice that covered Canada and the northern U.S. about 20,000 years ago and is now settling back. Factors such as these illustrate the advantages of remarkably accurate satellite technology now used in the determination of sea levels.

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17.14 PHENOMENA AT THE LAND–ATMOSPHERE INTERFACE

The interface between the atmosphere and land is a boundary of intense environmental activity. The combined effects of air and water tend to cause significant changes to the land materials at this interface. The top layer of exposed land is especially susceptible to physical and chemical weathering. Here, air laden with oxidant oxygen contacts rock, originally formed under reducing conditions, causing oxidation reactions to occur. Acid naturally present in rainwater as dissolved CO_2 or as pollutant sulfuric, sulfurous, nitric, or hydrochloric acid, can dissolve portions of some kinds of rocks. Organisms such as lichens, which consist of fungi and algae growing symbiotically on rock surfaces, drawing carbon dioxide, oxygen, or nitrogen from air, can grow on rock surfaces at the boundary of the atmosphere and geosphere, causing additional weathering to take place.

One of the most significant agents affecting exposed geospheric solids at the atmosphere/geosphere boundary is wind. Wind both erodes solids and acts as an agent to deposit solids on geospheric surfaces. The influence of wind is especially pronounced in dry areas. A major factor in wind erosion is wind **abrasions** in which solid particles of sand and rock carried by wind tend to wear away exposed rock and soil. Loose, unconsolidated sand and soil may be removed in large volumes by wind, a process called **deflation**.

The potential for wind to move matter is illustrated by the formation of large deposits of **loess**, consisting of finely divided soil carried by wind. Loess particles are typically several tens of micrometers in size, small enough to be carried great distances by wind. Especially common are loess deposits that originated with matter composed of rock ground to a fine flour by Ice Age glaciers. This material was first deposited in river valleys by flood waters issuing from melting glaciers, then blown some distance from the rivers by strong winds after drying out.

One of the more common geospheric features created by wind is a **dune**, consisting of a mound of debris, usually sand, dropped when wind slows down. As a dune builds, it forms an obstruction that slows wind even more, so that more sediment is dropped and, in the presence of sediment-laden wind, dunes several meters or more high may form rapidly. In forming a dune, heavier, coarser particles settle first so that the matter in dunes is sorted according to size, just like sediments deposited by flowing streams. In areas in which winds are prevalently from one direction, as is usually the case, dunes show a typical shape, as illustrated in Figure 17.11. It is seen that the steeply sloping side, called the **slip face**, is downwind.

Some of the environmental effects of dunes result from their tendency to migrate with the prevailing winds. Migration occurs as matter is blown by the wind up the gently sloping face of the dune and falls down the slip face. Migrating sand dunes have buried forest trees, and dust dunes in drought-stricken agricultural areas have filled road ditches, causing severely increased maintenance costs.

17.15 EFFECTS OF ICE

The power of ice to alter the geosphere is amply demonstrated by the remains of past glacial activity from the Ice Age. Those large areas of the earth's surface that

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were once covered with layers of glacial ice 1 or 2 kilometers in thickness show evidence of how the ice carved the surface, left massive piles of rock and gravel, and rich deposits of fresh water. The enormous weight of glaciers on earth's surface compressed it, and in places it is still springing back 10,000 or so years after the glaciers retreated. Today, the influence of ice on earth's surface is minimal, and there

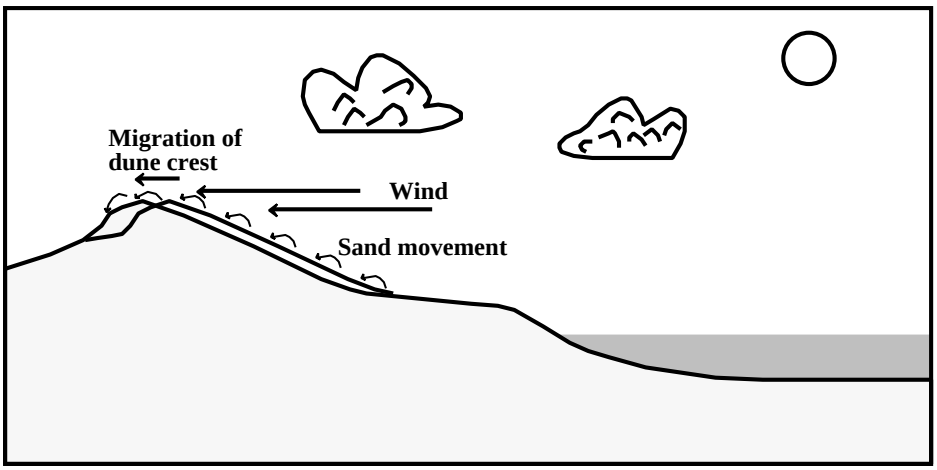


Figure 17.11 Shape and migration of a dune as determined by prevailing wind direction.

is substantial concern that melting of glaciers by greenhouse warming will raise sea levels so high that coastal areas will be inundated.

Glaciers form at sufficiently high latitudes and altitudes such that snow does not melt completely each summer. This occurs when snow becomes compacted over several to several thousand years such that the frozen water turns to crystals of true ice. Huge masses of ice with areas of several thousand square kilometers or more, and often around 1 kilometer thick, occur in polar regions and are called **continental glaciers**. Both Greenland and the Antarctic are covered by continental glaciers. **Alpine glaciers** occupy mountain valleys.

Heavy glaciers flow on a slope. This rate of flow is usually only a few meters per year, but may reach several kilometers per year. If a glacier flows into the sea, it may lose masses of ice as icebergs, a process called **calving**. Ice may also be lost by melting along the edges. The processes by which ice is lost are termed **ablation**.

Glacial ice affects the surface of the geosphere by both erosion and deposition. It is easy to imagine that a flowing mass of glacial ice is very efficient in scraping away the surface over which it flows, a process called **abrasion**. Adding to the erosive effect is the presence of rocks frozen into the glaciers that can act like tools to carve the surface of the underlying rock and soil. Whereas abrasion tends to wear rock surfaces away, producing a fine rock powder, larger bits of rock can be dislodged from the surface over which the glacier flows and be carried along with the glacial ice.

When glacial ice melts, the rock that has been incorporated into it is left behind. This material is called **till**, or if it has been carried for some distance by water running off the melting glacier it is called **outwash**. Piles of rock left by melting

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glaciers produce unique structures called **moraines**.

Although the effects of glaciers described above are the most spectacular manifestations of the action of ice on the geosphere, at a much smaller level, ice can have some very substantial effects. Freezing and expansion of water in pores and small crevices in rock are major contributors to physical weathering processes. Freeze/thaw cycles are also very destructive to some kinds of structures, such as stone buildings.

17.16 EFFECTS OF HUMAN ACTIVITIES

Human activities have profound effects on the geosphere. Such effects may be obvious and direct, such as strip mining, or rearranging vast areas for construction projects, such as roads and dams. Or the effects may be indirect, such as pumping so much water from underground aquifers that the ground subsides, or abusing soil such that it no longer supports plant life well and erodes. As the source of minerals and other resources used by humans, the geosphere is dug up, tunnelled, stripped bare, rearranged, and subjected to many other kinds of indignities. The land is often severely disturbed, air can be polluted with dust particles during mining, and water may be polluted. Many of these effects, such as soil erosion caused by human activities, are addressed elsewhere in this book.

Extraction of Geospheric Resources: Surface Mining

Many human effects on the geosphere result from extraction of resources from Earth's crust. The most damaging method of resource extraction is surface mining, employed in the United States to extract virtually all of the rock and gravel that is mined, well over half of the coal, and numerous other resources. Properly done, with appropriate restoration practices, surface mining does minimal damage and may even be used to improve surface quality, such as by the construction of surface reservoirs where rock or gravel have been extracted. In earlier times, before strict reclamation laws were in effect, surface mining, particularly of coal, left large areas of land scarred, devoid of vegetation, and subject to erosion.

Several approaches are employed in surface mining. Sand and gravel located under water are extracted by **dredging** with draglines or chain buckets attached to large conveyers. In most cases, resources are covered with an **overburden** of earthen material that does not contain any of the resource that is being sought. This material must be removed as **spoil**. **Open-pit mining** is, as the name implies, a procedure in which gravel, building stone, iron ore, and other materials are simply dug from a big hole in the ground. Some of these pits, such as several from which copper ore has been taken in the U. S., are truly enormous in size.

The best known (sometimes infamous) method of surface mining is **strip mining**, in which strips of overburden are removed by draglines and other heavy earth-moving equipment to expose seams of coal, phosphate rock, or other materials. Heavy equipment is used to remove a strip of overburden, and the exposed mineral resource is removed and hauled away. Overburden from a parallel strip is then removed and placed over the previously mined strip, and the procedure is repeated numerous times. Older practices left the replaced overburden as relatively steep erosion-prone banks. On highly sloping terrain, overburden is removed on progres-

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sively higher terraces and placed on the terrace immediately below.

Environmental Effects of Mining and Mineral Extraction

Some of the environmental effects of surface mining have been mentioned above. Although surface mining is most often considered for its environmental effects, subsurface mining can also have a number of effects, some of which are not immediately apparent and may be delayed for decades. Underground mines have a tendency to collapse, leading to severe subsidence. Mining disturbs groundwater aquifers. Water seeping through mines and mine tailings may become polluted. One of the more common and damaging effects of mining on water occurs when pyrite, FeS_2, commonly associated with coal, is exposed to air and becomes oxidized to sulfuric acid by bacterial action to produce acid mine water (see Chapter 12, Section 12.8). Some of the more damaging environmental effects of mining are the result of the processing of mined materials. Usually, ore is only part, often a small part, of the material that must be excavated. Various **beneficiation** processes are employed to separate the useful fraction of ore, leaving a residue of **tailings**. A number of adverse effects can result from environmental exposure of tailings. For example, residues left from the beneficiation of coal are often enriched in pyrite, FeS_2, which is oxidized microbiologically and chemically to produce damaging acidic drainage (acid mine water). Uranium ore tailings unwisely used as fill material have contaminated buildings with radioactive radon gas.

17.17 AIR POLLUTION AND THE GEOSPHERE

The geosphere can be a significant source of air pollutants, of which volcanic activity is one of the most common. Volcanic eruptions, fumaroles, hot springs, and geysers can emit toxic and acidic gases, including carbon monoxide, hydrogen chloride, and hydrogen sulfide. Greenhouse gas CO_2 and CH_4 can come from volcanic sources. Massive volcanic eruptions may inject huge amounts of particulate matter into the atmosphere. The incredibly enormous 1883 eruption of the East Indies volcano Krakatoa blew about 2.5 cubic kilometers of solid matter into the atmosphere, some of which penetrated well into the stratosphere. This material stayed aloft long enough to circle the earth several times, causing red sunsets and a measurable lowering of temperature worldwide.

The 1982 eruption of the southern Mexico volcano El Chicón showed the importance of the type of particulate matter in determining effects on climate. The matter given off by this eruption was unusually rich in sulfur, so that an aerosol of sulfuric acid formed and persisted in the atmosphere for about 3 years, during which time the mean global temperature was lowered by several tenths of a degree due to the presence of atmospheric sulfuric acid. By way of contrast, the eruption of Mt. St. Helens in Washington State in the U.S. 2 years earlier had little perceptible effect on climate, although the amount of material blasted into the atmosphere was about the same as that from El Chicón. The material from the Mt. St. Helens eruption had comparatively little sulfur in it, so the climatic effects were minimal.

Thermal smelting processes used to convert metal fractions in ore to usable forms have caused a number of severe air pollution problems that have affected the geosphere. Many metals are present in ores as sulfides, and smelting can release large quantities of sulfur dioxide, as well as particles that contain heavy metals such

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as arsenic, cadmium, or lead. The resulting acid and heavy metal pollution of surrounding land can cause severe damage to vegetation so that devastating erosion occurs. One such area is around a large nickel smelter in Sudbury, Ontario, Canada, where a large area of land has become denuded of vegetation. Similar dead zones have been produced by copper smelters in Tennessee and in eastern Europe, including the former Soviet Union.

Soil and its cultivation produces significant quantities of atmospheric emissions. Waterlogged soil, particularly that cultivated for rice, generates significant quantities of methane, a greenhouse gas. The microbial reduction of nitrate in soil releases nitrous oxide, N_2O, to the atmosphere. However, soil and rock can also remove atmospheric pollutants. It is believed that microorganisms in soil account for the loss from the atmosphere of some carbon monoxide, which some fungi and bacteria can metabolize. Carbonate rocks, such as calcium carbonate, $CaCO_3$, can neutralize acid from atmospheric sulfuric acid and acid gases.

As discussed in Section Chapter 14, Section 14.6, masses of atmospheric air can become trapped and stagnant under conditions of a temperature inversion in which the vertical circulation of air is limited by the presence of a relatively warm layer of air overlaying a colder layer at ground level. The effects of inversions can be aggravated by topographical conditions that tend to limit circulation of air. Figure 17.12 shows such a condition, in which surrounding mountain ridges limit horizontal air movement. Air pollutants may be forced up a mountain ridge from a polluted area to significantly higher altitudes than they would otherwise reach. Because of this "chimney effect," air pollutants may reach mountain pine forests that are particularly susceptible to damage from air pollutants such as ozone formed along with photochemical smog.

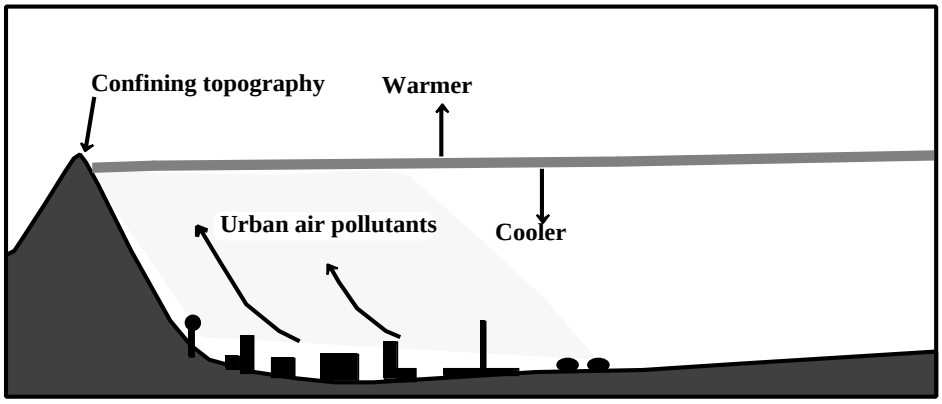


Figure 17.12 Topographical features, such as confining mountain ridges, may work with temperature inversions to increase the effects of air pollution.

17.18 WATER POLLUTION AND THE GEOSPHERE

Water pollution is addressed in detail elsewhere in this book. Much water pollution arises from interactions of groundwater and surface water with the geosphere. These aspects are addressed briefly here.

The relationship between water and the geosphere is twofold. The geosphere

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may be severely damaged by water pollution. This occurs, for example, when water pollutants produce contaminated sediments, such as those contaminated by heavy metals or PCBs. In some cases, the geosphere serves as a source of water pollutants. Examples include acid produced by exposed metal sulfides in the geosphere or synthetic chemicals improperly discarded in landfills.

The sources of water pollution are divided into two main categories. The first of these consists of **point sources**, which enter the environment at a single, readily identified entry point. An example of a point source would be a sewage-water outflow. Point sources tend to be those directly identified as to their origins from human activities. **Nonpoint sources** of pollution are those from broader areas. Such a source is water contaminated by fertilizer from fertilized agricultural land, or water contaminated with excess alkali leached from alkaline soils. Nonpoint sources are relatively harder to identify and monitor. Pollutants associated with the geosphere are usually nonpoint sources.

An especially common and damaging geospheric source of water pollutants consists of sediments carried by water from land into the bottoms of bodies of water. Most such sediments originate with agricultural land that has been disturbed such that soil particles are eroded from land into water. The most common manifestation of sedimentary material in water is opacity, which seriously detracts from the esthetics of the water and inhibits the growth of light-requiring algae. Sedimentary material deposited in reservoirs or canals can clog them and eventually make them unsuitable for water supply, flood control, navigation, and recreation. Suspended sediment in water used as a water supply can clog filters and add significantly to the cost of treating the water. Sedimentary material can devastate wildlife habitats by reducing food supplies and ruining nesting sites. Turbidity in water can severely curtail photosynthesis, thus reducing primary productivity necessary to sustain the food chains of aquatic ecosystems.

17.19 WASTE DISPOSAL AND THE GEOSPHERE

The geosphere receives many kinds and large amounts of wastes. Its ability to cope with such wastes with minimal damage is one of its most important characteristics and is dependent upon the kinds of wastes disposed on it. A variety of wastes, ranging from large quantities of relatively innocuous municipal refuse to much smaller quantities of potentially lethal radioactive wastes, are deposited on land or in landfills. These are addressed briefly in this section.

Municipal Refuse

The currently favored method for disposing of municipal solid wastes—household garbage—is in **sanitary landfills** (Figure 17.13) consisting of refuse piled on top of the ground or into a depression such as a valley, compacted, and covered at frequent intervals by soil. Frequent covering of the refuse with soil minimizes loss of blowing trash, water contamination, and other undesirable effects. A completed landfill can be put to beneficial uses, such as a recreational area; because of settling, gas production, and other factors, landfill surfaces are generally not suitable for building construction. Modern sanitary landfills are much preferable to the open

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dump sites that were once the most common means of municipal refuse disposal.

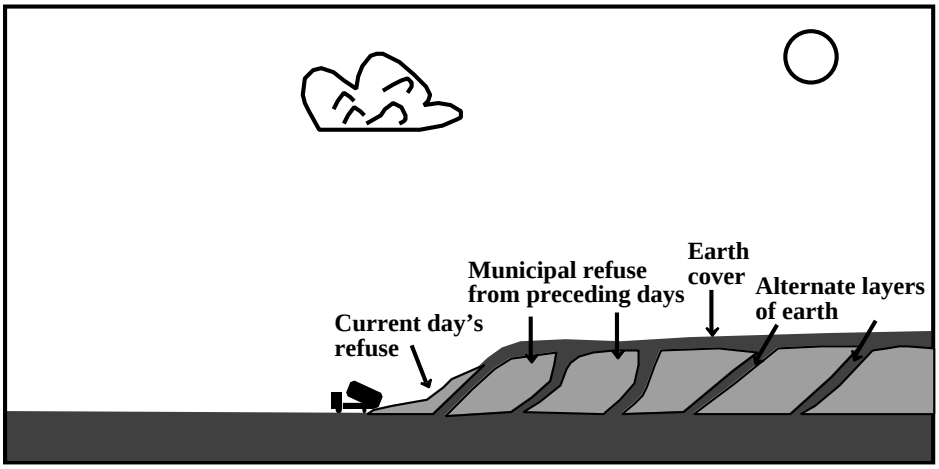


Figure 17.13 Structure of a sanitary landfill.

Although municipal refuse is much less dangerous than hazardous chemical waste, it still poses some hazards. Despite prohibitions against the disposal of cleaners, solvents, lead storage batteries, and other potentially hazardous materials in landfills, materials that pose some environmental hazards do find their way into landfills and can contaminate their surroundings.

Landfills produce both gaseous and aqueous emissions. Biomass in landfills quickly depletes oxygen by aerobic biodegradation of microorganisms in the landfill,

$$\{CH_2O\}(biomass) + O_2 \rightarrow CO_2 + H_2O \qquad (17.19.1)$$

emitting carbon dioxide. Over a period of many decades the buried biodegradable materials undergo anaerobic biodegradation,

$$2\{CH_2O\} \rightarrow CO_2 + CH_4 \qquad (17.19.2)$$

releasing methane as well as carbon dioxide. Although often impractical and too expensive, it is desirable to reclaim the methane as fuel, and some large sanitary landfills are major sources of methane. Released methane is a greenhouse gas and can pose significant explosion hazards to structures built on landfills. Although produced in much smaller quantities than methane, hydrogen sulfide, H_2S, is also generated by anaerobic biodegradation. This gas is toxic and has a bad odor. In a properly designed sanitary landfill, hydrogen sulfide releases are small and the gas tends to oxidize before it reaches the atmosphere in significant quantities.

Water infiltrating into sanitary landfills dissolves materials from the disposed refuse and runs off as **leachate**. Contaminated leachate is the single greatest potential pollution problem with refuse disposal sites, so it is important to minimize its production by designing landfills in a way that keeps water infiltration as low as possible. The anaerobic degradation of biomass produces organic acids that give the leachate a tendency to dissolve acid-soluble solutes, such as heavy metals. Leachate can infiltrate into groundwater, posing severe contamination problems. This is mini-

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mized by siting sanitary landfills over formations of poorly permeable clay or depositing layers of clay in the landfill before refuse is put into it. In addition, impermeable synthetic polymer liners may be placed in the bottom of the landfill. In areas of substantial rainfall, infiltration into the landfill exceeds its capacity to hold water so that leachate flows out. To prevent water pollution downstream, this leachate should be controlled and treated.

Hazardous chemical wastes are disposed of in so-called **secure landfills**, which are designed to prevent leakage and geospheric contamination of toxic chemicals disposed in them. Such a landfill is equipped with a variety of measures to prevent contamination of groundwater and the surrounding geosphere. The base of the landfill is made of compacted clay that is largely impermeable to leachate. An impermeable polymer liner is placed over the clay liner. The surface of the landfill is covered with material designed to reduce water infiltration, and the surface is designed with slopes that also minimize the amount of water running in. Elaborate drainage systems are installed to collect and treat leachate.

The most pressing matter pertaining to geospheric disposal of wastes involves radioactive wastes. Most of these wastes are **low-level** wastes, including discarded radioactive laboratory chemicals and pharmaceuticals, filters used in nuclear reactors, and ion-exchange resins used to remove small quantities of radionuclides from nuclear reactor cooler water. Disposed of in properly designed landfills, such wastes pose minimal hazards.

Of greater concern are the **high-level** radioactive wastes, primarily fission products of nuclear power reactors and byproducts of nuclear weapons manufacture. Many of these wastes are currently stored as solutions in tanks, many of which have outlived their useful lifetimes and pose leakage hazards, at sites such as the federal nuclear facility at Hanford, Washington, where plutonium was generated in large quantities during post-World War II years. Eventually, such wastes must be placed in the geosphere such that they will pose no hazards. Numerous proposals have been advanced for their disposal, including disposal in salt formations, subduction zones in the seafloor, and ice sheets. The most promising sites appear to be those in poorly permeable formations of igneous rock. Among these are basalts, which are strong, glassy igneous types of rock found in the Columbia River plateau. Granite and pyroclastic welded tuffs fused by past high temperature volcanic eruptions are also likely possibilities as sites for disposing of nuclear wastes and keeping them isolated for tens of thousands of years.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

That part of the earth upon which humans live and from which they extract most of their food, minerals, and fuels is called the [1]_____. A condition manifested by declining groundwater tables, salinization of topsoil and water, reduction of surface waters, unnaturally high soil erosion, and desolation of native

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vegetation is [2]_____. Earth's crust is [3]_____ _____. A naturally occurring inorganic solid with a definite internal crystal structure and chemical composition in the geosphere is a [4]_____, whereas a solid, cohesive mass of pure mineral or an aggregate of two or more minerals is a [5]_____. Some of the characteristics used to describe minerals are [6]_____ _____. There are only about [7]_____ rock-forming minerals, most of which are [8]_____. [9]_____ are formed by alteration of parent mineral matter, one of the most common classes of which are [10]_____. The chemical formula of halite is [11]_____ and it is an example of a class of minerals called [12]_____. The condensation of vapor-phase mineral constituents forms [13]_____. At elevated temperatures deep beneath earth's surface, rocks and mineral matter melt to produce a molten substance called [14]_____, which cools and solidifies to form [15]_____ _____ rock. Exposed to the atmosphere and water this kind of rock undergoes [16]_____ processes and eventually may be deposited as [17]_____ _____ rock, which may be converted by heat and pressure to [18]_____ rock. The processes by which rock is converted among the three kinds of rock just mentioned are described by the [19]_____. The mass movements of rocks to form continents, mountain ranges, and other huge features of the geosphere are described by the theory of [20]_____. Deformation and flow of solids and semisolids in the geosphere is described by [21]_____. The major kinds of processes that change the configuration of the geosphere can be divided into the two main categories of [22]_____. Two major kinds of internal processes are those that cause [23]_____ and those that result in the formation of [24]_____. Two harmful surface processes are [25]_____. The three kinds of "load" by which sedimentary materials may be carried by flowing water in streams are [26]_____. Clays may be defined as [27]_____ _____ _____. Clay minerals may attain a net negative charge by [28]_____, as a consequence of which these minerals hold and release [29]_____. [30]_____ deals with chemical species, reactions, and processes in the lithosphere and their interactions with the atmosphere and hydrosphere. As a chemical phenomenon, weathering can be viewed as [31]_____ _____. The major categories of chemical weathering are [32]_____ _____. The percentage of rock volume available to contain water is called its [33]_____ and the ease of flow of the water through the rock is called its [34]_____. Water present in a zone of saturation in mineral strata is called [35]_____. Two oxidation/reduction reactions that can clog the walls of water wells and impede the flow of water into the well are [36]___ _____. Tsunamis are [37] _____. A stream consists of [38]_____. A region along a

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stream that is periodically inundated by water overflowing the stream is [39]_____ _____. Extending from approximately the high tide mark to the dunes lining the landward edge of a beach is a relatively level area called the [40]_____. A major threat to coastal areas resulting from greenhouse warming is [41]_____ _____. Loess is produced by [42]_____ _____. When glacial ice melts, the rock that has been incorporated into it is left behind as a material called [43]_____, piles of which are called [44]_____. A method of surface mining in which strips of overburden are removed by draglines and other heavy earth-moving equipment to expose seams of coal, phosphate rock, or other materials is called [45]_____. [46]_____ processes are employed to separate the useful fraction of ore, leaving a residue called [47]_____. Sulfur-rich volcanic eruptions can result in the formation of [48]_____, which may [49]_____ global temperatures. Topographical conditions that tend to limit circulation of air can aggravate atmospheric conditions of [50]_____. Two general sources of water pollution based upon the entry of pollutants into water are [51]_____ _____. Landfills produce both [52]_____ emissions. Biomass in landfills quickly depletes [53]_____ by aerobic biodegradation of microorganisms in the landfill, after which [54]_____ may be generated. Water infiltrating into sanitary landfills dissolves materials from the disposed refuse and runs off as [55]_____. Hazardous chemical wastes are disposed of in so-called [56]_____, which are designed to prevent [57]
_____.

Answers to Chapter Summary

1. geosphere
2. desertification
3. the part of earth's outer skin that is accessible to humans
4. mineral
5. rock
6 crystal structure, crystal form, color, luster, streak, hardness, cleavage, fracture, and specific gravity
7. 25
8. silicates
9. Secondary minerals
10. clays
11. NaCl
12. evaporites
13. sublimates
14. magma
15. igneous
16. weathering
17. sedimentary
18. metamorphic
19. rock cycle

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20. plate tectonics
21. rheology
22. internal processes and surface processes

23. earthquakes
24. volcanoes
25. landslides and subsidence
26. dissolved, suspended, or bed load
27. a group of microcrystalline secondary minerals consisting of hydrous aluminum silicates that have sheet-like structures
28. ion replacement
29. exchangeable cations
30. Geochemistry
31. the result of the tendency of the rock/water/mineral system to attain equilibrium
32. hydration/dehydration, dissolution/precipitation, acid-base reactions, complexation, hydrolysis, and oxidation-reduction
33. porosity
34. permeability
35. groundwater
36. $4Fe^{2+}(aq) + O_2(aq) + 10H_2O \rightarrow 4Fe(OH)_3(s) + 8H^+$
 $2Mn^{2+}(aq) + O_2(aq) + (2x + 2)H_2O \rightarrow 2MnO_2 \cdot xH_2O(s) + 4H^+$
37. large ocean waves resulting from earthquake-induced movement of ocean floor.
38. water flowing through a channel
39. the floodplain
40. berm
41. raised ocean levels
42. the deposition of windblown soil
43. till
44. moraines
45. strip mining
46. Beneficiation
47. tailings
48. an aerosol of sulfuric acid
49. lower
50. temperature inversion
51. point and nonpoint sources
52. gaseous and aqueous
53. oxygen
54. methane
55. leachate
56. secure landfills
57. leakage and geospheric contamination of toxic chemicals disposed in them

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QUESTIONS AND PROBLEMS

1. Of the following, the one that is **not** a manifestation of desertification is (a) declining groundwater tables, (b) salinization of topsoil and water, (c) production of deposits of MnO_2 and $Fe_2O_3 \cdot H_2O$ from anaerobic processes, (d) reduction of surface waters, (e) unnaturally high soil erosion.

2. Give an example of how each of the following chemical or biochemical phenomena in soils operates to reduce the harmful nature of pollutants: (a) oxidation-reduction processes, (b) hydrolysis, (c) acid-base reactions, (d) precipitation, (e) sorption, (f) biochemical degradation.

3. Why do silicates and oxides predominate among earth's minerals?

4. Give the common characteristic of the minerals with the following formulas: NaCl, Na_2SO_4, $CaSO_4 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, $MgSO_4 \cdot 7H_2O$, $KMgClSO_4 \cdot {}^{11}/_{4}H_2O$, $K_2MgCa_2(SO_4)_4 \cdot 2H_2O$.

5. Explain how the following are related: weathering, igneous rock, sedimentary rock, soil.

6. Where does most flowing water that contains dissolved load originate? Why does it tend to come from this source?

7. What role might be played by water pollutants in the production of dissolved load and in the precipitation of secondary minerals from it?

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8. As defined in this chapter, are the ions involved in ion replacement the same as exchangeable cations? If not, why not?

9. Match the following:

A. Metamorphic rock	1. Produced by the precipitation or coagulation of dissolved or colloidal weathering products
B. Chemical sedimentary rocks	2. Contain residues of plant and animal remains
C. Detrital rock	3. Formed from action of heat and pressure on sedimentary rock
D. Organic sedimentary rocks	4. Formed from solid particles eroded from igneous rocks as a consequence of weathering

10. Speculate regarding how water present in poorly consolidated soil might add to the harm caused by earthquakes.

11. In what sense might volcanoes contribute to air pollution? What possible effects could this have on climate?

12. Explain how excessive pumping of groundwater might adversely affect streams, particularly in regard to the flow of small streams.

13. Which three elements are most likely to undergo oxidation as part of chemical weathering process? Give example reactions of each.

14. Match the following:

A. Groundwater	1. Water from precipitation in the form of rain or snow
B. Vadose water	2. Water present in a zone of saturation
C. Meteoric water	3. Water held in the unsaturated zone or zone of aeration
D. Water in capillary fringe	4. Water drawn somewhat above the water table by surface tension

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Fundamentals of Environmenal Chemistry
Boca Raton: CRC Press LLC, 2001

18 SOIL ENVIRONMENTAL CHEMISTRY

18.1 SOIL AND AGRICULTURE

Soil and agricultural practices are strongly tied with the environment. Some of these considerations are addressed later in this chapter along with a discussion of soil erosion and conservation. Cultivation of land and agricultural practices can influence both the atmosphere and the hydrosphere. Although this chapter deals primarily with soil, the topic of agriculture in general is introduced for perspective.

Agriculture

Agriculture, the production of food by growing crops and livestock, provides for the most basic of human needs. No other industry impacts as much as agriculture does on the environment. Agriculture is absolutely essential to the maintenance of the huge human populations now on earth. The displacement of native plants, destruction of wildlife habitat, erosion, pesticide pollution, and other environmental aspects of agriculture have enormous potential for environmental damage. Survival of humankind on earth demands that agricultural practice become as environmentally friendly as possible. On the other hand, growth of domestic crops removes (at least temporarily) greenhouse gas carbon dioxide from the atmosphere and provides potential sources of renewable resources of energy and fiber that can substitute for petroleum-derived fuels and materials.

Agriculture can be divided into the two main categories of **crop farming**, in which plant photosynthesis is used to produce grain, fruit, and fiber, and **livestock farming**, in which domesticated animals are grown for meat, milk, and other animal products. The major divisions of crop farming include production of cereals, such as wheat, corn or rice; animal fodder, such as hay; fruit; vegetables; and specialty crops, such as sugarcane, pineapple, sugar beets, tea, coffee, tobacco, cotton, and cacao. Livestock farming involves the raising of cattle, sheep, goats, swine, asses, mules, camels, buffalo, and various kinds of poultry. In addition to meat, livestock produce dairy products, eggs, wool, and hides. Freshwater fish and even crayfish are raised on "fish farms." Beekeeping provides honey.

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Agriculture is based on domestic plants engineered from their wild plant ancestors by early farmers. Without perhaps much of an awareness of what they were doing, they selected plants with desired characteristics for the production of food. This selection of plants for domestic use brought about a very rapid evolutionary change, so profound that the products often barely resemble their wild ancestors. Plant breeding based on scientific principles of heredity is a very recent development dating from early in the present century. One of the major objectives of plant breeding has been to increase yield. An example of success in this area is the selection of dwarf varieties of rice, which yield much better and mature faster than the varieties that they replaced. Such rice was largely responsible for the "green revolution" dating from about the 1950s. Yields of crops can also be increased by selecting for resistance to insects, drought, and cold. In some cases, the goal is to increase nutritional value, such as in the development of corn high in lysine, an amino acid essential for human nutrition, such that corn becomes a more complete food.

The development of hybrids has vastly increased yields and other desired characteristics of a number of important crops. Basically, **hybrids** are the offspring of crosses between two different **true-breeding** strains. Often quite different from either parent strain, hybrids tend to exhibit "hybrid vigor" and to have significantly higher yields. The most success with hybrid crops has been obtained with corn (maize). Corn is one of the easiest plants to hybridize because of the physical separation of the male flowers, which grow as tassels on top of the corn plant, from female flowers, which are attached to incipient ears on the side of the plant. Despite past successes by more conventional means and some early disappointments with "genetic engineering," application of recombinant DNA technology (Section 18.10) will probably eventually overshadow all the advances ever made in plant breeding.

In addition to plant strains and varieties, numerous other factors are involved in crop production. Weather is an obvious factor, and shortages of water, chronic in many areas of the world, are mitigated by irrigation. Here, automated techniques and computer control are beginning to play an important, more environmentally friendly role by minimizing the quantities of water required. The application of chemical fertilizer has vastly increased crop yields. The judicious application of pesticides, especially herbicides, but including insecticides and fungicides as well, has increased crop yields and reduced losses greatly. Use of herbicides has had an environmental benefit in reducing the degree of mechanical cultivation of soil required. Indeed, "no-till" and "low-till" agriculture are now widely practiced on a large scale.

The crops that provide for most of human caloric food intake, as well as much food for animals, are **cereals**, which are harvested for their starch-rich seeds. In addition to corn, mentioned above, wheat used for making bread and related foods, and rice consumed directly, other major cereal crops include barley, oats, rye, sorghum, and millet. As applied to agriculture and food, **vegetables** are plants or their products that can be eaten directly by humans. A large variety of different parts of plants are consumed as vegetables. These include leaves (lettuce), stems (asparagus), roots (carrots), tubers (potato), bulb (onion), immature flower (broccoli), immature fruit (cucumber), mature fruit (tomato), and seeds (pea). Fruits, which are bodies of plant tissue containing the seed, can be viewed as a subclassification of vegetables. Common fruits include apple, peach, apricot, citrus (orange, lemon, lime, grapefruit), banana, cherry, and various kinds of berries.

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The rearing of domestic animals can have significant environmental effects. The Netherlands' pork industry has been so productive that hog manure and its by-products have caused serious problems. Overflow from waste lagoons associated with hog production caused very damaging water pollution in eastern North Carolina following the record rainfall from Hurricane Floyd in September 1999. Goats and sheep have destroyed pastureland in the Near East, Northern Africa, Portugal, and Spain. Of particular concern are the environmental effects of raising cattle. Significant amounts of forest land have been converted to marginal pasture land to raise beef. Production of one pound of beef requires about four times as much water and four times as much feed as does production of one pound of chicken. An interesting aspect of the problem is emission of greenhouse-gas methane by anaerobic bacteria in the digestive systems of cattle and other ruminant animals; cattle rank right behind wetlands and rice paddies as producers of atmospheric methane. However, because of the action of specialized bacteria in their stomachs, cattle and other ruminant animals are capable of converting otherwise unusable cellulose to food.

Pesticides and Agriculture

Pesticides, particularly insecticides and herbicides, are an integral part of modern agricultural production. In the United States, agricultural pesticides are regulated under the Federal Insecticide, Fungicide, and Rodenticide (FIFRA) act, first passed in 1947, revised in a major way in 1972, and subjected to several amendments since then. Starting in 1989 under FIFRA, pre-1972 pesticides were required to undergo reregistration. Since this process began, manufacturers have withdrawn from the market several thousand products because of the expense of the safety review process. The problem has been especially severe for **minor-use pesticides** for which the market is not very large. In contrast to pesticides used on approximately 220 million acres of major crops in the U.S.—corn, soybeans, wheat, and cotton—minor-use pesticides are applied on only about 8 million acres of orchards, trees, ornamental plants, turf grass, fruits, nuts, and vegetables. Despite their limited use, about 40% of the monetary value of agricultural pesticides resides with minor-use pesticides. Complicating the reregistration process for many years was the well-intentioned but unrealistic 1958 Delaney Amendment to the Food, Drug, and Cosmetic Act which prohibited in food any chemical that had been shown to cause cancer in animals and humans. Many chemicals that are almost certainly safe as trace-level contaminants in food will, indeed, cause cancer when fed in massive doses to experimental animals. This effect has been attributed in part to the fact that huge doses of some chemicals destroy tissue, which the organism attempts to replace by growing new cells. Cells that are reproducing rapidly in an attempt to make up for tissue loss are more likely to become cancerous.

An interesting development regarding the use of herbicides in the late 1990s was the production of transgenic crops resistant to specific herbicides. The Monsanto company pioneered this approach with the development of "Roundup Ready" crops that resist the herbicidal effects of Monsanto's flagship Roundup® herbicide, a glyphosate compound with an annual market exceeding $2 billion. The seedlings of crops resistant to the herbicide are not harmed by exposure to it, whereas competing

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weeds are killed. In an interesting marketing strategy, Monsanto has licensed manufacturing and distribution rights for Roundup to other companies for application onto “Roundup Ready” crops sold by Monsanto.

Soil

Soil, consisting of a finely divided layer of weathered minerals and organic matter upon which plants grow, is the most fundamental requirement for agriculture. To humans and most terrestrial organisms, soil is the most important part of the geosphere. Though only a tissue-thin layer compared with the earth’s total diameter, soil is the medium that produces most of the food required by most living things. Good soil—and a climate conducive to its productivity—is the most valuable asset a nation can have.

In addition to being the site of most food production, soil is the receptor of large quantities of pollutants, such as particulate matter from power plant smokestacks. Fertilizers, pesticides, and some other materials applied to soil often contribute to water and air pollution. Therefore, soil is a key component of environmental chemical cycles.

Soils are formed by the weathering of parent rocks as the result of interactive geological, hydrological, and biological processes (see Chapter 15). Soils are porous and are vertically stratified into horizons as the result of downward-percolating water and biological processes, including the production and decay of biomass. Soils are open systems that undergo continual exchange of matter and energy with the atmosphere, hydrosphere, and biosphere.

18.2 NATURE AND COMPOSITION OF SOIL

Soil is a variable mixture of minerals, organic matter, and water capable of supporting plant life on the earth’s surface. It is the final product of the weathering action of physical, chemical, and biological processes on rocks, which largely produces clay minerals. The organic portion of soil consists of plant biomass in various stages of decay. High populations of bacteria, fungi, and animals such as earthworms can be found in soil. Soil contains air spaces and generally has a loose texture (Figure 18.1).

The solid fraction of typical productive soil is approximately 5% organic matter and 95% inorganic matter. Some soils, such as peat soils, may contain as much as 95% organic material. Other soils contain as little as 1% organic matter.

Typical soils exhibit distinctive layers with increasing depth (Figure 18.2). These layers are called **horizons**. Horizons form as the result of complex interactions among processes that occur during weathering. Rainwater percolating through soil carries dissolved and colloidal solids to lower horizons where they are deposited. Biological processes, such as bacterial decay of residual plant biomass, produces slightly acidic CO_2, organic acids, and complexing compounds that are carried by rainwater to lower horizons, where they interact with clays and other minerals, altering the properties of the minerals. The top layer of soil, typically several inches in thickness, is known as the A horizon, or **topsoil**. This is the layer of maximum biological activity in the soil and contains most of the soil organic matter. Metal ions

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and clay particles in the A horizon are subject to considerable leaching. The next layer is the B horizon, or **subsoil**. It receives material such as organic matter, salts, and clay particles leached from the topsoil. The C horizon is composed of weathered parent rocks from which the soil originated.

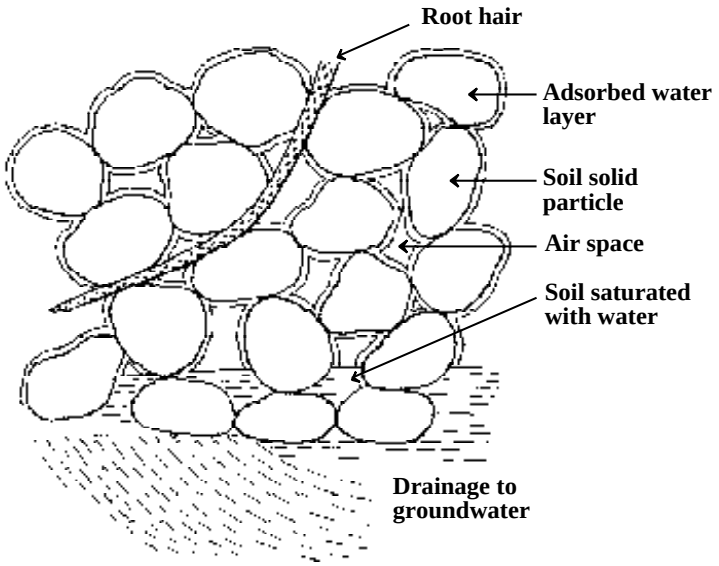


Figure 18.1 Fine structure of soil, showing solid, water, and air phases.

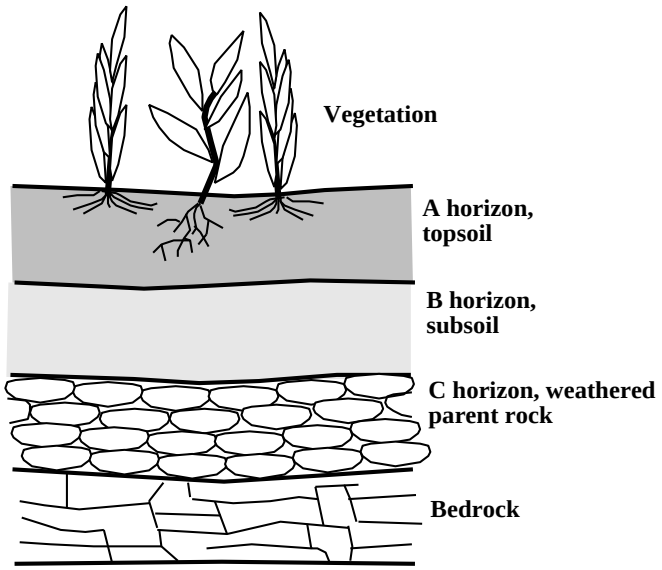


Figure 18.2 Soil profile showing soil horizons.

Soils exhibit a large variety of characteristics that are used for their classification for various purposes, including crop production, road construction, and waste disposal. Soil profiles are discussed above. The parent rocks from which soils are

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formed obviously play a strong role in determining the composition of soils. Other soil characteristics include strength, workability, soil particle size, permeability, and degree of maturity. One of the more important classes of productive soils is the **podzol** type of soil formed under relatively high rainfall conditions in temperate zones of the world. These generally rich soils tend to be acidic (pH 3.5–4.5) such that alkali and alkaline earth metals and, to a lesser extent aluminum and iron, are leached from their A horizons, leaving kaolinite as the predominant clay mineral. At somewhat higher pH in the B horizons, hydrated iron oxides and clays are redeposited.

From the engineering standpoint, especially, the mechanical properties of soil are emphasized. These properties, which may have important environmental implications in areas such as waste disposal, are largely determined by particle size. According to the United Classification System (UCS), the four major categories of soil particle sizes are the following: Gravels (2–60 mm) > sands (0.06–2 mm) > silts (0.06-0.006 mm) > clays (less than 0.002 mm). In the UCS classification scheme clays represent a size fraction rather than a specific class of mineral matter.

Water and Air in Soil

Large quantities of water are required for the production of most plant materials. For example, several hundred kg of water are required to produce one kg of dry hay. Water is part of the three-phase, solid-liquid-gas system making up soil. It is the basic transport medium for carrying essential plant nutrients from solid soil particles into plant roots and to the farthest reaches of the plant's leaf structure (Figure 18.3). The water enters the atmosphere from the plant's leaves, a process called **transpiration**.

Normally, because of the small size of soil particles and the presence of small capillaries and pores in the soil, the water phase is not totally independent of soil solid matter. The availability of water to plants is governed by gradients arising from capillary and gravitational forces. The availability of nutrient solutes in water depends upon concentration gradients and electrical potential gradients. Water present in larger spaces in soil is relatively more available to plants and readily drains away. Water held in smaller pores or between the unit layers of clay particles is held much more strongly. Soils high in organic matter may hold appreciably more water than other soils, but it is relatively less available to plants because of physical and chemical sorption of the water by the organic matter.

There is a very strong interaction between clays and water in soil. Water is absorbed on the surfaces of clay particles. Because of the high surface-volume ratio of colloidal clay particles, a great deal of water can be bound in this manner. Water is also held between the unit layers of the expanding clays, such as the montmorillonite clays. As soil becomes waterlogged (water-saturated) it undergoes drastic changes in physical, chemical, and biological properties. Oxygen in such soil is rapidly used up by the respiration of microorganisms that degrade soil organic matter. In such soils, the bonds holding soil colloidal particles together are broken, which causes disruption of soil structure. Thus, the excess water in such soils is detrimental to plant growth, and the soil does not contain the air required by most plant roots. Most useful crops, with the notable exception of rice, cannot grow on waterlogged soils.

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One of the most marked chemical effects of waterlogging is a reduction of pE by the action of organic reducing agents acting through bacterial catalysts. Thus, the redox condition of the soil becomes much more reducing, and the soil pE may drop

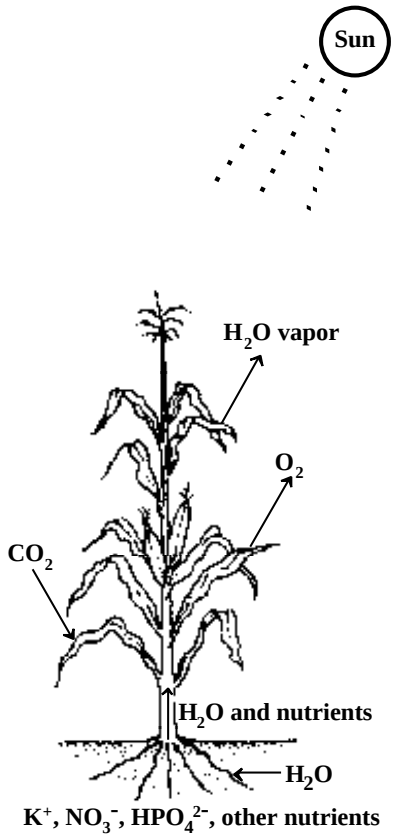


Figure 18.3 Plants transport water from the soil to the atmosphere by transpiration. Nutrients are also carried from the soil to the plant extremities by this process. Plants remove CO_2 from the atmosphere and add O_2 by photosynthesis. The reverse occurs during plant respiration.

from that of water in equilibrium with air (+13.6 at pH 7) to 1 or less. One of the more significant results of this change is the mobilization of iron and manganese as soluble iron(II) and manganese(II) through reduction of their insoluble higher oxides:

$$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O \quad (18.2.1)$$

$$Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 3H_2O \quad (18.2.2)$$

Although soluble manganese generally is found in soil as Mn^{2+} ion, soluble iron(II) frequently occurs as negatively charged iron-organic chelates. Strong chelation of iron(II) by soil fulvic acids (Chapter 3) apparently enables reduction of iron(III) oxides at more positive pE values than would otherwise be possible. This causes an upward shift in the Fe(II)-$Fe(OH)_3$ boundary shown in Figure 4.4.

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Some soluble metal ions such as Fe^{2+} and Mn^{2+} are toxic to plants at high levels. Their oxidation to insoluble oxides may cause formation of deposits of Fe_2O_3 and MnO_2, which clog tile drains in fields.

Roughly 35% of the volume of typical soil is composed of air-filled pores. Whereas the normal dry atmosphere at sea level contains 21% O_2 and 0.03% CO_2 by volume, these percentages may be quite different in soil air because of the decay of organic matter:

$$\{CH_2O\} + O_2 \rightarrow CO_2 + H_2O \qquad (18.2.3)$$

This process consumes oxygen and produces CO_2. As a result, the oxygen content of air in soil may be as low as 15%, and the carbon dioxide content may be several percent. Thus, the decay of organic matter in soil increases the equilibrium level of dissolved CO_2 in groundwater. This lowers the pH and contributes to weathering of carbonate minerals, particularly calcium carbonate (see Reaction 3.7.6). As discussed in Section 18.3, CO_2 also shifts the equilibrium of the process by which roots absorb metal ions from soil.

The Inorganic Components of Soil

The weathering of parent rocks and minerals to form the inorganic soil components results ultimately in the formation of inorganic colloids. These colloids are repositories of water and plant nutrients, which may be made available to plants as needed. Inorganic soil colloids often absorb toxic substances in soil, thus playing a role in detoxification of substances that otherwise would harm plants. The abundance and nature of inorganic colloidal material in soil are obviously important factors in determining soil productivity.

The uptake of plant nutrients by roots often involves complex interactions with the water and inorganic phases. For example, a nutrient held by inorganic colloidal material has to traverse the mineral/water interface and then the water/root interface. This process is often strongly influenced by the ionic structure of soil inorganic matter.

As noted in Section 17.2, the most common elements in the earth's crust are oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium. Therefore, minerals composed of these elements—particularly silicon and oxygen—constitute most of the mineral fraction of the soil. Common soil mineral constituents are finely divided quartz (SiO_2), orthoclase ($KAlSi_3O_8$), albite ($NaAlSi_3O_8$), epidote ($4CaO{\cdot}3(AlFe)_2O_3{\cdot}6SiO_2{\cdot}H_2O$), geothite ($FeO(OH)$), magnetite ($Fe_3O_4$), calcium and magnesium carbonates ($CaCO_3$, $CaCO_3{\cdot}MgCO_3$), and oxides of manganese and titanium.

Organic Matter in Soil

Though typically composing less than 5% of a productive soil, organic matter largely determines soil productivity. It serves as a source of food for micro-organisms, undergoes chemical reactions such as ion exchange, and influences the physical properties of soil. Some organic compounds even contribute to the weathering of mineral matter, the process by which soil is formed. For example, $C_2O_4^{2-}$, oxalate ion, produced as a soil fungi metabolite, occurs in soil as the calcium

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salts whewellite and weddelite. Oxalate in soil water dissolves minerals, thus speeding the weathering process and increasing the availability of nutrient ion species. This weathering process involves oxalate complexation of iron or aluminum in minerals, represented by the reaction

$$3H^+ + M(OH)_3(s) + 2CaC_2O_4(s) \rightarrow M(C_2O_4)_2^-(aq) + 2Ca^{2+}(aq) + 3H_2O \qquad (18.2.4)$$

in which M is Al or Fe. Some soil fungi produce citric acid and other chelating organic acids that react with silicate minerals and release potassium and other nutrient metal ions held by these minerals.

The strong chelating agent 2-ketogluconic acid is produced by some soil bacteria. By solubilizing metal ions, it may contribute to the weathering of minerals. It may also be involved in the release of phosphate from insoluble phosphate compounds.

Biologically active components of the organic soil fraction include polysaccharides, amino sugars, nucleotides, and organic sulfur and phosphorus compounds. Humus, a water-insoluble material that biodegrades very slowly, makes up the bulk of soil organic matter. The organic compounds in soil are summarized in Table 18.1.

Table 18.1 Major Classes of Organic Compounds in Soil

Compound type	Composition	Significance
Humus	Degradation-resistant residue from plant decay, largely C, H, and O	Most abundant organic component, improves soil physical properties, exchanges nutrients, reservoir of fixed N
Fats, resins, and waxes	Lipids extractable by organic solvents	Generally, only several percent of soil organic matter, may adversely affect soil physical properties by repelling water, perhaps phytotoxic
Saccharides	Cellulose, starches, hemicellulose, gums	Major food source for soil microorganisms, help stabilize soil aggregates
N-containing organics	Nitrogen bound to humus, amino acids, amino sugars, other compounds	Provide nitrogen for soil fertility
Phosphorus compounds	Phosphate esters, inositol phosphates (phytic acid), phospholipids	Sources of plant phosphate

The accumulation of organic matter in soil is strongly influenced by temperature and by the availability of oxygen. Since the rate of biodegradation decreases with decreasing temperature, organic matter does not degrade rapidly in colder climates and tends to build up in soil. In water and in waterlogged soils, decaying vegetation

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does not have easy access to oxygen, and organic matter accumulates. The organic content may reach 90% in areas where plants grow and decay in soil saturated with water.

The presence of naturally occurring polynuclear aromatic (PAH) compounds is an interesting feature of soil organic matter. These compounds, some of which are carcinogenic, are discussed as air pollutants in Sections 10.8 and 12.4. PAH compounds found in soil include fluoranthene, pyrene, and chrysene. PAH compounds in soil result in part from combustion from both natural sources (grass fires) or pollutant sources. Terpenes also occur in soil organic matter. Extraction of soil with ether and alcohol yields the pigments β-carotene, chlorophyll, and xanthophyll.

Soil Humus

Of the organic components listed in Table 18.1, **soil humus** is by far the most significant. Humus, composed of a base-soluble fraction called humic and fulvic acids (described in Section 11.9), and an insoluble fraction called humin, is the residue left when bacteria and fungi biodegrade plant material. The bulk of plant biomass consists of relatively degradable cellulose and degradation-resistant lignin, which is a polymeric substance with a higher carbon content than cellulose. Among lignin's prominent chemical components are aromatic rings connected by alkyl chains, methoxyl groups, and hydroxyl groups. These structural artifacts occur in soil humus and give it many of its characteristic properties.

The process by which humus is formed is called **humification**. Soil humus is similar to its lignin precursors, but has more carboxylic acid groups. Part of each molecule of humic substance is nonpolar and hydrophobic, and part is polar and hydrophilic. Such molecules are called **amphiphiles**, and they form micelles (see Section 5.4 and Figure 5.4), in which the nonpolar parts compose the inside of small colloidal particles and the polar functional groups are on the outside. Amphiphilic humic substances probably also form bilayer surface coatings on mineral grains in soil.

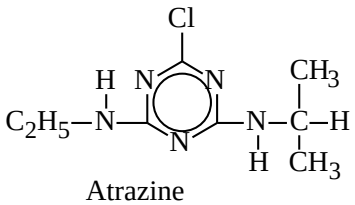
An increase in nitrogen-carbon ratio is a significant feature of the transformation of plant biomass to humus through the humification process. This ratio starts at approximately 1/100 in fresh plant biomass. During humification, microorganisms convert organic carbon to CO_2 to obtain energy. Simultaneously, the bacterial action incorporates bound nitrogen with the compounds produced by the decay processes. The result is a nitrogen-carbon ratio of about 1/10 upon completion of humification. As a general rule, therefore, humus is relatively rich in organically bound nitrogen.

Humic substances influence soil properties to a degree out of proportion to their small percentage in soil. They strongly bind metals, and serve to hold micronutrient metal ions in soil. Because of their acid-base character, humic substances serve as buffers in soil. The water-holding capacity of soil is significantly increased by humic substances. These materials also stabilize aggregates of soil particles, and increase the sorption of organic compounds by soil.

Humic materials in soil strongly sorb many solutes in soil water and have a particular affinity for heavy polyvalent cations. Soil humic substances may contain levels of uranium more than 10^4 times that of the water with which they are in equilibrium. Thus, water becomes depleted of its cations (or purified) in passing through humic-rich soils. Humic substances in soils also have a strong affinity for organic

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compounds with low water solubility, such as DDT or Atrazine, a herbicide widely used to kill weeds in corn fields.



Atrazine

In some cases, there is a strong interaction between the organic and inorganic portions of soil. This is especially true of the strong complexes formed between clays and humic (fulvic) acid compounds. In many soils, 50–100% of soil carbon is complexed with clay. These complexes play a role in determining the physical properties of soil, soil fertility, and stabilization of soil organic matter. One of the mechanisms for the chemical binding between clay colloidal particles and humic organic particles is probably of the flocculation type (see Chapter 5) in which anionic organic molecules with carboxylic acid functional groups serve as bridges in combination with cations to bind clay colloidal particles together as a floc. Support is given to this hypothesis by the known ability of NH_4^+, Al^{3+}, Ca^{2+}, and Fe^{3+} cations to stimulate clay-organic complex formation. The synthesis, chemical reactions, and biodegradation of humic materials are affected by interaction with clays. The lower-molecular-weight fulvic acids may be bound to clay, occupying spaces in layers in the clay.

The Soil Solution

The **soil solution** is the aqueous portion of soil that contains dissolved matter from soil chemical and biochemical processes in soil and from exchange with the hydrosphere and biosphere. This medium transports chemical species to and from soil particles and provides intimate contact between the solutes and the soil particles. In addition to providing water for plant growth, it is an essential pathway for the exchange of plant nutrients between roots and solid soil.

Obtaining a sample of soil solution is often very difficult because the most significant part of it is bound in capillaries and as surface films. The most straightforward means is collection of drainage water. Soil solution can be isolated from moist solid soil by displacement with a water-immiscible fluid, mechanical separation by centrifugation, or pressure or vacuum treatment.

Dissolved mineral matter in soil is largely present as ions. Prominent among the cations are H^+, Ca^{2+}, Mg^{2+}, K^+, Na^+, and usually very low levels of Fe^{2+}, Mn^{2+}, and Al^{3+}. The last three cations may be present in partially hydrolized form, such as $FeOH^+$, or complexed by organic humic substance ligands. Anions that may be present are HCO_3^-, CO_3^{2-}, HSO_4^-, SO_4^{2-}, Cl^-, and F^-. In addition to being bound to H^+ in species such as bicarbonate, anions may be complexed with metal ions, such as in AlF^{2+}. Multivalent cations and anions form ion pairs with each other in soil solutions. Examples of these are $CaSO_4$ and $FeSO_4$.

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18.3 ACID-BASE AND ION EXCHANGE REACTIONS IN SOILS

One of the more important chemical functions of soils is the exchange of cations. As discussed in Chapter 5, the ability of a sediment or soil to exchange cations is expressed as the cation-exchange capacity (CEC), the number of milliequivalents (meq) of monovalent cations that can be exchanged per 100 g of soil (on a dry-weight basis). The CEC should be looked upon as a conditional constant since it can vary with soil conditions such as pE and pH. Both the mineral and organic portions of soils exchange cations. Clay minerals exchange cations because of the presence of negatively charged sites on the mineral, resulting from the substitution of an atom of lower oxidation number for one of higher number, for example, magnesium for aluminum. Organic materials exchange cations because of the presence of the carboxylate group and other basic functional groups. Humus typically has a very high cation-exchange capacity. The cation-exchange capacity of peat can range from 300–400 meq/100 g. Values of cation-exchange capacity for soils with more typical levels of organic matter are around 10–30 meq/100 g.

Cation exchange in soil is the mechanism by which potassium, calcium, magnesium, and essential trace-level metals are made available to plants. When nutrient metal ions are taken up by plant roots, hydrogen ion is exchanged for the metal ions. This process, plus the leaching of calcium, magnesium, and other metal ions from the soil by water containing carbonic acid, tends to make the soil acidic:

$$\text{Soil}\}Ca^{2+} + 2CO_2 + 2H_2O \rightarrow \text{Soil}\}(H^+)_2 + Ca^{2+}(\text{root}) + 2HCO_3^- \quad (18.3.1)$$

Soil acts as a buffer and resists changes in pH. The buffering capacity depends upon the type of soil.

Production of Mineral Acid in Soil

The oxidation of pyrite in soil causes formation of acid-sulfate soils sometimes called “cat clays”:

$$FeS_2 + {}^7/_2O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-} \quad (18.3.2)$$

Cat clay soils can have pH values as low as 3.0. These soils, which are commonly found in Delaware, Florida, New Jersey, and North Carolina, are formed when neutral or basic marine sediments containing FeS_2 become acidic upon oxidation of pyrite when exposed to air. For example, soil reclaimed from marshlands and used for citrus groves has developed high acidity detrimental to plant growth. In addition, H_2S released by reaction of FeS_2 with acid is very toxic to citrus roots.

Soils are tested for potential acid-sulfate formation using a peroxide test. This test consists of oxidizing FeS_2 in the soil with 30% H_2O_2,

$$FeS_2 + {}^{15}/_2H_2O_2 \rightarrow Fe^{3+} + H^+ + 2SO_4^{2-} + 7H_2O \quad (18.3.3)$$

then testing for acidity and sulfate. Appreciable levels of sulfate and a pH below 3.0 indicate potential to form acid-sulfate soils. If the pH is above 3.0, either little FeS_2 is present or sufficient $CaCO_3$ is in the soil to neutralize the H_2SO_4 and acidic Fe^{3+}.

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Pyrite-containing mine spoils (residue left over from mining) also form soils similar to acid-sulfate soils of marine origin. In addition to high acidity and toxic H_2S, a major chemical species limiting plant growth on such soils is Al(III). Aluminum ion liberated in acidic soils is very toxic to plants.

Adjustment of Soil Acidity

Most common plants grow best in soil with a pH near neutrality. If the soil becomes too acidic for optimum plant growth, it may be restored to productivity by liming, ordinarily through the addition of calcium carbonate:

$$\text{Soil}\}(H^+)_2 + CaCO_3 \rightarrow \text{Soil}\}Ca^{2+} + CO_2 + H_2O \qquad (18.3.4)$$

In areas of low rainfall, soils may become too basic (alkaline) due to the presence of basic salts such as Na_2CO_3. Alkaline soils can be treated with aluminum or iron sulfate, which release acid on hydrolysis:

$$2Fe^{3+} + 3SO_4^{2-} + 6H_2O \rightarrow 2Fe(OH)_3(s) + 6H^+ + 3SO_4^{2-} \qquad (18.3.5)$$

Sulfur added to soils is oxidized by bacterially mediated reactions to sulfuric acid:

$$S + {}^3/_2O_2 + H_2O \rightarrow 2H^+ + SO_4^{2-} \qquad (18.3.6)$$

and sulfur is used, therefore, to acidify alkaline soils. The huge quantities of sulfur now being removed from fossil fuels to prevent air pollution by sulfur dioxide may make the treatment of alkaline soils by sulfur much more attractive economically.

Ion Exchange Equilibria in Soil

Competition of different cations for cation exchange sites on soil cation exchangers may be described semiquantitatively by exchange constants. For example, soil reclaimed from an area flooded with seawater will have most of its cation exchange sites occupied by Na^+, and restoration of fertility requires binding of nutrient cations such as K^+:

$$\text{Soil}\}Na^+ + K^+ \leftarrow\rightarrow \text{Soil}\}K^+ + Na^+ \qquad (18.3.7)$$

The exchange constant is K_C,

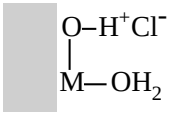
$$K_C = \frac{N_K[Na^+]}{N_{Na}[K^+]} \qquad (18.3.8)$$

which expresses the relative tendency of soil to retain K^+ and Na^+. In this equation, N_K and N_{Na} are the equivalent ionic fractions of potassium and sodium, respectively, bound to soil, and $[Na^+]$ and $[K^+]$ are the concentrations of these ions in the surrounding soil water. For example, a soil with all cation exchange sites

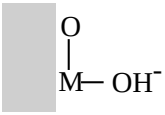
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occupied by Na^+ would have a value of 1.00 for N_{Na}; with one-half of the cation exchange sites occupied by Na^+, N_{Na} is 0.5; etc. The exchange of anions by soil is not nearly so clearly defined as is the exchange of cations. In many cases, the exchange of anions does not involve a simple ion-exchange process. This is true of the strong retention of orthophosphate species by soil. At the other end of the scale, nitrate ion is very weakly retained by the soil.

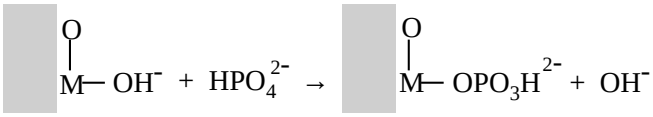
Anion exchange can be visualized as occurring at the surfaces of oxides in the mineral portion of soil. A mechanism for the acquisition of surface charge by metal oxides is shown in Chapter 5, Figure 5.5, using MnO_2 as an example. At low pH, a metal oxide surface may have a net positive charge enabling it to hold anions, such as chloride, by electrostatic attraction as shown below where M represents a metal:



At higher pH values, the metal oxide surface has a net negative charge due to the formation of OH^- ion on the surface caused by loss of H^+ from the water molecules bound to the surface:



In such cases, it is possible for anions such as HPO_4^{2-} to displace hydroxide ion and bond directly to the oxide surface:



(18.3.9)

18.4 MACRONUTRIENTS IN SOIL

One of the most important functions of soil in supporting plant growth is to provide essential plant nutrients—macronutrients and micronutrients. Macronutrients are those elements that occur in substantial levels in plant materials or in fluids in the plant. Micronutrients (Section 18.6) are elements that are essential only at very low levels and generally are required for the functioning of essential enzymes.

The elements generally recognized as essential macronutrients for plants are carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, magnesium, and sulfur. Carbon, hydrogen, and oxygen are obtained from the atmosphere. The other essential macronutrients must be obtained from soil. Of these, nitrogen, phosphorus, and potassium are the most likely to be lacking and are commonly added to soil as fertilizers. Because of their importance, these elements are discussed separately in Section 18.5.

Calcium-deficient soils are relatively uncommon. Application of lime, a process used to treat acid soils (see Section 18.3), provides a more than adequate calcium supply for plants. However, calcium uptake by plants and leaching by carbonic acid

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(Reaction 18.3.1) may produce a calcium deficiency in soil. Acid soils may still contain an appreciable level of calcium which, because of competition by hydrogen ion, is not available to plants. Treatment of acid soil to restore the pH to near-neutrality generally remedies the calcium deficiency. In alkaline soils, the presence of high levels of sodium, magnesium, and potassium sometimes produces calcium deficiency because these ions compete with calcium for availability to plants.

Most of the 2.1% of magnesium in earth's crust is rather strongly bound in minerals. Exchangeable magnesium held by ion-exchanging organic matter or clays is considered available to plants. The availability of magnesium to plants depends upon the calcium/magnesium ratio. If this ratio is too high, magnesium may not be available to plants and magnesium deficiency results. Similarly, excessive levels of potassium or sodium may cause magnesium deficiency.

Sulfur is assimilated by plants as the sulfate ion, SO_4^{2-}. In addition, in areas where the atmosphere is contaminated with SO_2, sulfur may be absorbed as sulfur dioxide by plant leaves. Atmospheric sulfur dioxide levels have been high enough to kill vegetation in some areas (see Chapter 11). However, some experiments designed to show SO_2 toxicity to plants have resulted in increased plant growth where there was an unexpected sulfur deficiency in the soil used for the experiment.

Soils deficient in sulfur do not support plant growth well, largely because sulfur is a component of some essential amino acids and of thiamin and biotin. Sulfate ion is generally present in the soil as immobilized insoluble sulfate minerals, or as soluble salts that are readily leached from the soil and lost as soil water runoff. Unlike the case of nutrient cations such as K^+, little sulfate is adsorbed to the soil (that is, bound by ion exchange binding) where it is resistant to leaching while still available for assimilation by plant roots.

Soil sulfur deficiencies have been found in a number of regions of the world. Whereas most fertilizers used to contain sulfur, its use in commercial fertilizers has declined. With continued use of sulfur-deficient fertilizers, it is possible that sulfur will become a limiting nutrient in more cases.

As noted in Section 18.3, the reaction of FeS_2 with acid in acid-sulfate soils may release H_2S, which is very toxic to plants and which also kills many beneficial microorganisms. Toxic hydrogen sulfide can also be produced by reduction of sulfate ion through microorganism-mediated reactions with organic matter. Production of hydrogen sulfide in flooded soils may be inhibited by treatment with oxidizing compounds, one of the most effective of which is KNO_3.

18.5 NITROGEN, PHOSPHORUS, AND POTASSIUM IN SOIL

Nitrogen, phosphorus, and potassium are plant nutrients that are obtained from soil. They are so important for crop productivity that they are commonly added to soil as fertilizers. The environmental chemistry of these elements is discussed here and their production as fertilizers in Section 18.7.

Nitrogen

Figure 18.4 summarizes the primary sinks and pathways of nitrogen in soil. In most soils, over 90% of the nitrogen content is organic. This organic nitrogen is

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primarily the product of the biodegradation of dead plants and animals. It is eventually hydrolyzed to NH_4^+, which can be oxidized to NO_3^- by the action of bacteria in the soil.

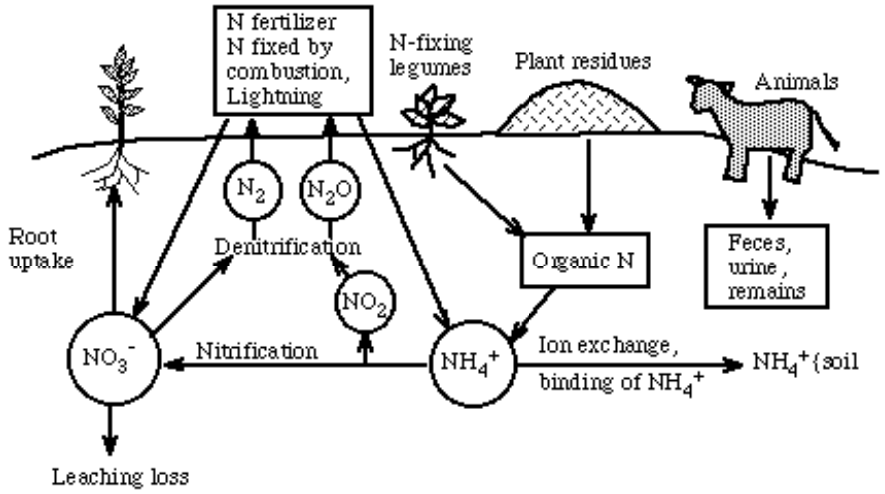


Figure 18.4 Nitrogen sinks and pathways in soil.

Nitrogen bound to soil humus is especially important in maintaining soil fertility. Unlike potassium or phosphate, nitrogen is not a significant product of mineral weathering. Nitrogen-fixing organisms ordinarily cannot supply sufficient nitrogen to meet peak demand. Inorganic nitrogen from fertilizers and rainwater is often largely lost by leaching. Soil humus, however, serves as a reservoir of nitrogen required by plants. It has the additional advantage that its rate of decay, hence its rate of nitrogen release to plants, roughly parallels plant growth—rapid during the warm growing season, slow during the winter months.

Nitrogen is an essential component of proteins and other constituents of living matter. Plants and cereals grown on nitrogen-rich soils not only provide higher yields, but are often substantially richer in protein and, therefore, more nutritious. Nitrogen is most generally available to plants as nitrate ion, NO_3^-. Some plants such as rice may utilize ammonium nitrogen; however, other plants are poisoned by this form of nitrogen. When nitrogen is applied to soils in the ammonium form, nitrifying bacteria perform an essential function in converting it to available nitrate ion.

Plants may absorb excessive amounts of nitrate nitrogen from soil. This phenomenon occurs particularly in heavily fertilized soils under drought conditions. Forage crops containing excessive amounts of nitrate can poison ruminant animals such as cattle or sheep. Plants having excessive levels of nitrate can endanger people when used for ensilage, an animal food consisting of finely chopped plant material such as partially matured whole corn plants, fermented in a structure called a silo. Under the reducing conditions of fermentation, nitrate in ensilage may be reduced to toxic NO_2 gas, which can accumulate to high levels in enclosed silos. There have been many cases reported of persons being killed by accumulated NO_2 in silos.

Nitrogen fixation is the process by which atmospheric N_2 is converted to nitrogen compounds available to plants. Human activities are resulting in the fixation

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of a great deal more nitrogen than would otherwise be the case. Artificial sources now account for 30-40% of all nitrogen fixed. These include chemical fertilizer manufacture, nitrogen fixed during fuel combustion, combustion of nitrogen-containing fuels, and the increased cultivation of nitrogen-fixing legumes (see the following paragraph). A major concern with this increased fixation of nitrogen is the possible effect upon the atmospheric ozone layer by N_2O released during denitrification of fixed nitrogen.

Before the widespread introduction of nitrogen fertilizers, soil nitrogen was provided primarily by legumes. These are plants such as soybeans, alfalfa, and clover, which contain on their root structures bacteria capable of fixing atmospheric nitrogen. Leguminous plants have a symbiotic (mutually advantageous) relationship with the bacteria that provide their nitrogen. Legumes may add significant quantities of nitrogen to soil, up to 10 pounds per acre per year, which is comparable to amounts commonly added as synthetic fertilizers. Soil fertility with respect to nitrogen can be maintained by rotating plantings of nitrogen-consuming plants with plantings of legumes, a fact recognized by agriculturists as far back as the Roman era.

The nitrogen-fixing bacteria in legumes exist in special structures on the roots called root nodules (see Fig. 18.5). The rod-shaped bacteria that fix nitrogen are members of a special genus, *Rhizobium*. These bacteria can exist independently, but cannot fix nitrogen except in symbiotic combination with plants. Although all species of *Rhizobium* appear to be very similar, they exhibit a great deal of specificity in their choice of host plants. Curiously, legume root nodules also contain a form of hemoglobin, which must somehow be involved in the nitrogen-fixation process.

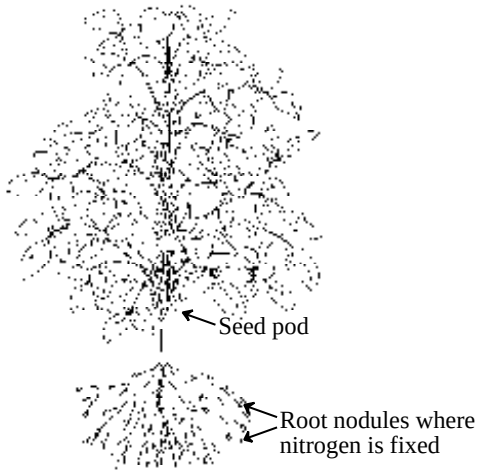


Figure 18.5 A soybean plant, showing root nodules where nitrogen is fixed.

Nitrate pollution of some surface waters and groundwater has become a major problem in some agricultural areas (see Chapter 7). Although fertilizers have been implicated in such pollution, there is evidence that feedlots are a major source of nitrate pollution. The growth of livestock populations and the concentration of livestock in feedlots have aggravated the problem. Such concentrations of cattle, coupled with the fact that a steer produces approximately 18 times as much waste

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material as a human, have resulted in high levels of water pollution in rural areas with small human populations. Streams and reservoirs in such areas frequently are just as polluted as those in densely populated and highly industrialized areas.

Nitrate in farm wells is a common and especially damaging manifestation of nitrogen pollution from feedlots because of the susceptibility of ruminant animals to nitrate poisoning. The stomach contents of ruminant animals such as cattle and sheep constitute a reducing medium (low pE) and contain bacteria capable of reducing nitrate ion to toxic nitrite ion:

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O \quad (18.5.1)$$

The origin of most nitrate produced from feedlot wastes is amino nitrogen present in nitrogen-containing waste products. Approximately one-half of the nitrogen excreted by cattle is contained in the urine. Part of this nitrogen is proteinaceous and the other part is in the form of urea, NH_2CONH_2. As a first step in the degradation process, the amino nitrogen is probably hydrolyzed to ammonia, or ammonium ion:

$$RNH_2 + H_2O \rightarrow R\text{-}OH + NH_3\,(NH_4^+) \quad (18.5.2)$$

This product is then oxidized through microorganism-catalyzed reactions to nitrate ion:

$$NH_3 + 2O_2 \rightarrow H^+ + NO_3^- + H_2O \quad (18.5.3)$$

Under some conditions, an appreciable amount of the nitrogen originating from the degradation of feedlot wastes is present as ammonium ion. Ammonium ion is rather strongly bound to soil (recall that soil is a generally good cation exchanger), and a small fraction is fixed as nonexchangeable ammonium ion in the crystal lattice of clay minerals. Because nitrate ion is not strongly bound to soil, it is readily carried through soil formations by water. Many factors, including soil type, moisture, and level of organic matter, affect the production of ammonia and nitrate ion originating from feedlot wastes, and a marked variation is found in the levels and distributions of these materials in feedlot areas.

Phosphorus

Although the percentage of phosphorus in plant material is relatively low, it is an essential component of plants. Phosphorus, like nitrogen, must be present in a simple inorganic form before it can be taken up by plants. In the case of phosphorus, the utilizable species is some form of orthophosphate ion. In the pH range that is present in most soils, $H_2PO_4^-$ and HPO_4^{2-} are the predominant orthophosphate species.

Orthophosphate is most available to plants at pH values near neutrality. It is believed that in relatively acidic soils, orthophosphate ions are precipitated or sorbed by species of Al(III) and Fe(III). In alkaline soils, orthophosphate may react with calcium carbonate to form relatively insoluble hydroxyapatite:

$$3HPO_4^{2-} + 5CaCO_3(s) + 2H_2O \rightarrow Ca_5(PO_4)_3(OH)(s) + 5HCO_3^- + OH^- \quad (18.5.4)$$

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In general, because of these reactions, little phosphorus applied as fertilizer leaches from the soil. This is important from the standpoint of both water pollution and utilization of phosphate fertilizers.

Potassium

Relatively high levels of potassium are utilized by growing plants. Potassium activates some enzymes and plays a role in the water balance in plants. It is also essential for some carbohydrate transformations. Crop yields are generally greatly reduced in potassium-deficient soils. The higher the productivity of the crop, the more potassium is removed from soil. When nitrogen fertilizers are added to soils to increase productivity, removal of potassium is enhanced. Therefore, potassium may become a limiting nutrient in soils heavily fertilized with other nutrients.

Potassium is one of the most abundant elements in the earth's crust, of which it makes up 2.6%; however, much of this potassium is not easily available to plants. For example, some silicate minerals such as leucite, $K_2O \cdot Al_2O_3 \cdot 4SiO_2$, contain strongly bound potassium. Exchangeable potassium held by clay minerals is relatively more available to plants.

18.6 MICRONUTRIENTS IN SOIL

Boron, chlorine, copper, iron, manganese, molybdenum (for N-fixation), and zinc are considered essential plant **micronutrients**. These elements are needed by plants only at very low levels and frequently are toxic at higher levels. There is some chance that other elements will be added to this list as techniques for growing plants in environments free of specific elements improve. Most of these elements function as components of essential enzymes. Manganese, iron, chlorine, and zinc may be involved in photosynthesis.Though not established for all plants, it is possible that sodium, silicon, and cobalt may also be essential plant nutrients.

Iron and manganese occur in a number of soil minerals. Sodium and chlorine (as chloride) occur naturally in soil and are transported as atmospheric particulate matter from marine sprays (see Chapter 10). Some of the other micronutrients and trace elements are found in primary (unweathered) minerals that occur in soil. Boron is substituted isomorphically for Si in some micas and is present in tourmaline, a mineral with the formula $NaMg_3Al_6B_3Si_6O_{27}(OH,F)_4$. Copper is isomorphically substituted for other elements in feldspars, amphiboles, olivines, pyroxenes, and micas; it also occurs as trace levels of copper sulfides in silicate minerals. Molybdenum occurs as molybdenite (MoS_2). Vanadium is isomorphically substituted for Fe or Al in oxides, pyroxenes, amphiboles, and micas. Zinc is present as the result of isomorphic substitution for Mg, Fe, and Mn in oxides, amphiboles, olivines, and pyroxenes and as trace zinc sulfide in silicates. Other trace elements that occur as specific minerals, sulfide inclusions, or by isomorphic substitution for other elements in minerals are chromium, cobalt, arsenic, selenium, nickel, lead, and cadmium.

The trace elements listed above may be coprecipitated with secondary minerals (see Section 17.2) that are involved in soil formation. Such secondary minerals include oxides of aluminum, iron, and manganese (precipitation of hydrated oxides of iron and manganese very efficiently removes many trace metal ions from solution); calcium and magnesium carbonates; smectites; vermiculites; and illites.

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Some plants accumulate extremely high levels of specific trace metals. Those accumulating more than 1.00 mg/g of dry weight are called **hyperaccumulators**. Nickel and copper both undergo hyperaccumulation in some plant species. As an example of a metal hyperaccumulater, *Aeolanthus biformifolius DeWild*, growing in copper-rich regions of Shaba Province, Zaire, contains up to 1.3% copper (dry weight) and is known as a "copper flower."

The hyperaccumulation of metals by some plants has led to the idea of **phytoremediation** in which plants growing on contaminated ground accumulate metals, which are then removed with the plant biomass. *Brassica juncea* and *Brassica chinensis* (Chinese cabbage) have been shown to hyperaccumulate as much as 5 grams of uranium per kg plant dry weight when grown on uranium-contaminated soil. Uranium accumulation in the plants was enhanced by the addition of citrate, which complexes uranium and makes it more soluble.

18.7 FERTILIZERS

Crop fertilizers contain nitrogen, phosphorus, and potassium as major components. Magnesium, sulfate, and micronutrients may also be added. Fertilizers are designated by numbers, such as 6-12-8, showing the respective percentages of nitrogen expressed as N (in this case 6%), phosphorus as P_2O_5 (12%), and potassium as K_2O (8%). Farm manure corresponds to an approximately 0.5-0.24-0.5 fertilizer. The organic fertilizers such as manure must undergo biodegradation to release the simple inorganic species (NO_3^-, $H_xPO_4^{x-3}$, K^+) assimilable by plants.

Most modern nitrogen fertilizers are made by the Haber process, in which N_2 and H_2 are combined over a catalyst at temperatures of approximately 500˚C and pressures up to 1000 atm:

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (18.7.1)$$

The anhydrous ammonia product has a very high nitrogen content of 82%. It can be added directly to the soil, for which it has a strong affinity because of its water solubility and formation of ammonium ion:

$$NH_3(g)\ (\text{water}) \rightarrow NH_3(aq) \qquad (18.7.2)$$

$$NH_3(aq) + H_2O \rightarrow NH_4^+ + OH^- \qquad (18.7.3)$$

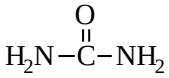
Special equipment is required, however, because of the toxicity of ammonia gas. Aqua ammonia, a 30% solution of NH_3 in water, can be used with much greater safety. It is sometimes added directly to irrigation water. It should be pointed out that ammonia vapor is toxic and NH_3 is reactive with some substances. Improperly discarded or stored ammonia can be a hazardous waste.

Ammonium nitrate, NH_4NO_3, is a common solid nitrogen fertilizer. It is made by oxidizing ammonia over a platinum catalyst, converting the nitric oxide product to nitric acid, and reacting the nitric acid with ammonia. The molten ammonium nitrate product is forced through nozzles at the top of a *prilling tower* and solidifies to form small pellets while falling through the tower. The particles are coated with a water repellent. Ammonium nitrate contains 33.5% nitrogen. Although convenient to apply

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to soil, it requires considerable care during manufacture and storage because it is explosive. Ammonium nitrate also poses some hazards. It is mixed with fuel oil to form an explosive that serves as a substitute for dynamite in quarry blasting and construction. This mixture was used to devastating effect in the dastardly bombing of the Oklahoma City Federal Building in 1995.

Urea,



is easier to manufacture and handle than ammonium nitrate. It is now the favored solid nitrogen-containing fertilizer. The overall reaction for urea synthesis is

$$CO_2 + 2NH_3 \rightarrow CO(NH_2)_2 + H_2O \qquad (18.7.4)$$

involving a rather complicated process in which ammonium carbamate, chemical formula $NH_2CO_2NH_4$, is an intermediate.

Other compounds used as nitrogen fertilizers include sodium nitrate (obtained largely from Chilean deposits, see Section 17.2), calcium nitrate, potassium nitrate, and ammonium phosphates. Ammonium sulfate, a by-product of coke ovens, used to be widely applied as fertilizer. The alkali metal nitrates tend to make soil alkaline, whereas ammonium sulfate leaves an acidic residue.

Phosphate minerals are found in several states, including Idaho, Montana, Utah, Wyoming, North Carolina, South Carolina, Tennessee, and Florida. The principal mineral is fluorapatite, $Ca_5(PO_4)_3F$. The phosphate from fluorapatite is relatively unavailable to plants, and fluorapatite is frequently treated with phosphoric or sulfuric acids to produce superphosphates:

$$2Ca_5(PO_4)_3F(s) + 14H_3PO_4 + 10H_2O \rightarrow 2HF(g) + 10Ca(H_2PO_4)_2{\cdot}H_2O \qquad (18.7.5)$$

$$2Ca_5(PO_4)_3F(s) + 7H_2SO_4 + 3H_2O \rightarrow 2HF(g) + 3Ca(H_2PO_4)_2{\cdot}H_2O + 7CaSO_4 \qquad (18.7.6)$$

The superphosphate products are much more soluble than the parent phosphate minerals. The HF produced as a byproduct of superphosphate production can create air pollution problems.

Phosphate minerals are rich in trace elements required for plant growth, such as boron, copper, manganese, molybdenum, and zinc. Ironically, these elements are lost to a large extent when the phosphate minerals are processed to make fertilizer. Ammonium phosphates are excellent, highly soluble phosphate fertilizers. Liquid ammonium polyphosphate fertilizers consisting of ammonium salts of pyrophosphate, triphosphate, and small quantities of higher polymeric phosphate anions in aqueous solution work very well as phosphate fertilizers. The polyphosphates are believed to have the additional advantage of chelating iron and other micronutrient metal ions, thus making the metals more available to plants.

Potassium fertilizer components consist of potassium salts, generally KCl. Such salts are found as deposits in the ground or can be obtained from some brines. Very

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large deposits are found in Saskatchewan, Canada. These salts are all quite soluble in water. One problem encountered with potassium fertilizers is the luxury uptake of potassium by some crops, which absorb more potassium than is really needed for their maximum growth. In a crop where only the grain is harvested, leaving the rest of the plant in the field, luxury uptake does not create much of a problem because most of the potassium is returned to the soil with the dead plant. However, when hay or forage is harvested, potassium contained in the plant as a consequence of luxury uptake is lost from the soil.

18.8 WASTES AND POLLUTANTS IN SOIL

Soil receives large quantities of waste products. Much of the sulfur dioxide emitted in the burning of sulfur-containing fuels ends up as soil sulfate. Atmospheric nitrogen oxides are converted to nitrates in the atmosphere, and the nitrates eventually are deposited on soil. Soil sorbs NO and NO_2, and these gases are oxidized to nitrate in the soil. Carbon monoxide is converted to CO_2 and possibly to biomass by soil bacteria and fungi. Particulate lead from automobile exhausts is found at elevated levels in soil along heavily traveled highways. Elevated levels of lead from lead mines and smelters are found on soil near such facilities.

Soil is the receptor of many hazardous wastes from landfill leachate, lagoons, and other sources (see Section 19.13). In some cases, land farming of degradable hazardous organic wastes is practiced as a means of disposal and degradation. The degradable material is worked into the soil, and soil microbial processes bring about its degradation. As discussed in Chapter 8, sewage and fertilizer-rich sewage sludge can be applied to soil.

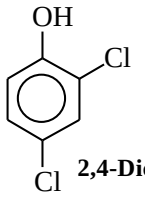
Volatile organic compounds (VOC) such as benzene, toluene, xylenes, dichloromethane, trichloroethane, and trichloroethylene, may contaminate soil in industrialized and commercialized areas, particularly in countries in which enforcement of regulations is not very stringent. One of the more common sources of these contaminants is leaking underground storage tanks. Landfills built before current stringent regulations were enforced, and improperly discarded solvents are also significant sources of soil VOCs.

Measurements of levels of polychlorinated biphenyls (PCBs) in soils that have been archived for several decades provide interesting insight into the contamination of soil by pollutant chemicals and subsequent loss of these substances from soil. Analyses of soils from the United Kingdom dating from the early 1940s to 1992 showed that the PCB levels increased sharply from the 1940s, reaching peak levels around 1970. Subsequently, levels fell sharply and now are back to early 1940s concentrations. This fall was accompanied by a shift in distribution to the more highly chlorinated PCBs, which was attributed by those doing the study to volatilization and long range transport of the lighter PCBs away from the soil. These trends parallel levels of PCB manufacture and use in the United Kingdom from the early 1940s to the present. This is consistent with the observation that relatively high concentrations of PCBs have been observed in remote Arctic and sub-Arctic regions, attributed to condensation in colder climates of PCBs volatilized in warmer regions.

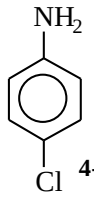
Some pollutant organic compounds are believed to become bound with humus during the humification process that occurs in soil. This largely immobilizes and

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detoxifies the compounds. Binding of pollutant compounds by humus is particularly likely to occur with compounds that have structural similarities to humic substances, such as phenolic and anilinic compounds, illustrated by the following two examples:



2,4-Dichlorophenol

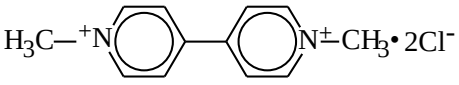


4-Chloroaniline

Such compounds can become covalently bonded to humic substance molecules, largely through the action of microbial enzymes. After binding they are known as **bound residues** and are highly resistant to extraction with solvents by procedures that would remove unbound parent compounds. Compounds in the bound residues are resistant to biological and chemical attack.

Soil receives enormous quantities of pesticides as an inevitable result of their application to crops. The degradation and eventual fate of these pesticides on soil largely determines their ultimate environmental effects. Detailed knowledge of these effects are now required for licensing of a new pesticide (in the U.S. under the Federal Insecticide, Fungicide, and Rodenticide act, FIFRA). Among the factors to be considered are the sorption of the pesticide by soil; leaching of the pesticide into water, as related to its potential for water pollution; effects of the pesticide on microorganisms and animal life in the soil; and possible production of relatively more toxic degradation products.

Adsorption by soil is a key aspect of pesticide degradation and plays a strong role in the speed and degree of degradation. The degree of adsorption and the speed and extent of ultimate degradation are influenced by a number of other factors. Some of these, including solubility, volatility, charge, polarity, and molecular structure and size, are properties of the medium. Adsorption of a pesticide by soil components may have several effects. Under some circumstances, it retards degradation by separating the pesticide from the microbial enzymes that degrade it, whereas under other circumstances the reverse is true. Purely chemical degradation reactions may be catalyzed by adsorption. Loss of the pesticide by volatilization or leaching is diminished. The toxicity of a herbicide to plants may be reduced by sorption on soil. The forces holding a pesticide to soil particles may be of several types. Physical adsorption involves van der Waals forces arising from dipole-dipole interactions between the pesticide molecule and charged soil particles. Ion exchange is especially effective in holding cationic organic compounds, such as the herbicide paraquat,

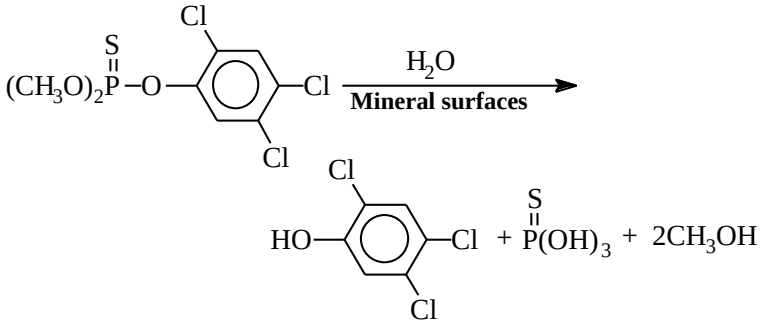


to anionic soil particles. Some neutral pesticides become cationic by protonation and are bound as the protonated positive form. Hydrogen bonding is another mechanism by which some pesticides are held to soil. In some cases, a pesticide may act as a ligand coordinating to metals in soil mineral matter.

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The three primary ways in which pesticides are degraded in or on soil are *chemical degradation, photochemical reactions,* and, most important, *biodegradation.* Various combinations of these processes may operate in the degradation of a pesticide.

Chemical degradation of pesticides has been observed experimentally in soils and clays sterilized to remove all microbial activity. For example, clays have been shown to catalyze the hydrolysis of *o,o*-dimethyl-*o*-2,4,5-trichlorophenyl thiophosphate (also called Trolene, Ronnel, Etrolene, or trichlorometafos), an effect attributed to -OH groups on the mineral surface:



(18.8.1)

Many other purely chemical hydrolytic reactions of pesticides occur in soil.

A number of pesticides have been shown to undergo **photochemical reactions**, that is, chemical reactions brought about by the absorption of light (see Chapter 14). Frequently, isomers of the pesticides are formed as products. Many of the studies reported apply to pesticides in water or on thin films, and the photochemical reactions of pesticides on soil and plant surfaces remain largely a matter of speculation.

Biodegradation and the Rhizosphere

Although insects, earthworms, and plants may play roles in the **biodegradation** of pesticides and other pollutant organic chemicals, microorganisms have the most important role. Several examples of microorganism-mediated degradation of organic chemical species are given in Chapter 11.

The **rhizosphere**, the layer of soil in which plant roots are especially active, is a particularly important part of soil with respect to biodegradation of wastes. It is a zone of increased biomass and is strongly influenced by the plant root system and the microorganisms associated with plant roots. The rhizosphere may have more than ten times the microbial biomass per unit volume than nonrhizospheric zones of soil. This population varies with soil characteristics, plant and root characteristics, moisture content, and exposure to oxygen. If this zone is exposed to pollutant compounds, microorganisms adapted to their biodegradation may also be present.

Plants and microorganisms exhibit a strong synergistic relationship in the rhizosphere, which benefits the plant and enables highly elevated populations of rhizospheric microorganisms to exist. Epidermal cells sloughed from the root as it grows and carbohydrates, amino acids, and root-growth-lubricant mucigel secreted from the roots all provide nutrients for microorganism growth. Root hairs provide a hospitable biological surface for colonization by microorganisms.

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The biodegradation of a number of synthetic organic compounds has been demonstrated in the rhizosphere. Understandably, studies in this area have focused on herbicides and insecticides that are widely used on crops. Among the organic species for which enhanced biodegradation in the rhizosphere has been demonstrated are the following (associated plant or crop shown in parentheses): 2,4-D herbicide (wheat, African clover, sugarcane, flax), parathion (rice, bush bean), carbofuran (rice), atrazine (corn), diazinon (wheat, corn, peas), volatile aromatic alkyl and aryl hydrocarbons and chlorocarbons (reeds), and surfactants (corn, soybean, cattails). It is interesting to note that enhanced biodegradation of polycyclic aromatic hydrocarbons (PAH) was observed in the rhizospheric zones of prairie grasses. This observation is consistent with the fact that in nature such grasses burn regularly and significant quantities of PAH compounds are deposited on soil as a result.

18.9 SOIL LOSS AND DEGRADATION

Soil is a fragile resource that can be lost by erosion or become so degraded that it is no longer useful to support crops. The physical properties of soil and, hence, its susceptibility to erosion, are strongly affected by the cultivation practices to which the soil is subjected. **Desertification** refers to the process associated with drought and loss of fertility by which soil becomes unable to grow significant amounts of plant life. Desertification caused by human activities is a common problem globally, occurring in diverse locations such as Argentina, the Sahara, Uzbekistan, the U.S. Southwest, Syria, and Mali. It is a very old problem dating back many centuries to the introduction of domesticated grazing animals to areas where rainfall and groundcover were marginal. The most notable example is desertification aggravated by domesticated goats in the Sahara region. Desertification involves a number of interrelated factors, including erosion, climate variations, water availability, loss of fertility, loss of soil humus, and deterioration of soil chemical properties.

A related problem is **deforestation**, loss of forests. The problem is particularly acute in tropical regions, where the forests contain most of the existing plant and animal species. In addition to extinction of these species, deforestation can cause devastating deterioration of soil through erosion and loss of nutrients.

Soil erosion can occur by the action of both water and wind, although water is the primary source of erosion. Millions of tons of topsoil are carried by the Mississippi River and swept from its mouth each year. About one-third of U.S. topsoil has been lost since cultivation began on the continent. At the present time, approximately one-third of U.S. cultivated land is eroding at a rate sufficient to reduce soil productivity. It is estimated that 48 million acres of land, somewhat more than 10 percent of that under cultivation, is eroding at unacceptable levels, taken to mean a loss of more than 14 tons of topsoil per acre each year. Specific areas in which the greatest erosion is occurring include northern Missouri, southern Iowa, west Texas, western Tennessee, and the Mississippi Basin. Figure 18.6 shows the pattern of soil erosion in the continental U.S. in 1977.

Problems involving soil erosion were aggravated in the 1970s and early 1980s when high prices for farmland resulted in the intensive cultivation of high-income crops, particularly corn and soybeans. These crops grow in rows with bare soil in between, which tends to wash away with each rainfall. Furthermore, the practice of

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planting corn and soybeans year after year without intervening plantings of soil-restoring clover or grass became widespread. The problem of decreased productivity due to soil erosion has been masked somewhat by increased use of chemical fertilizers.

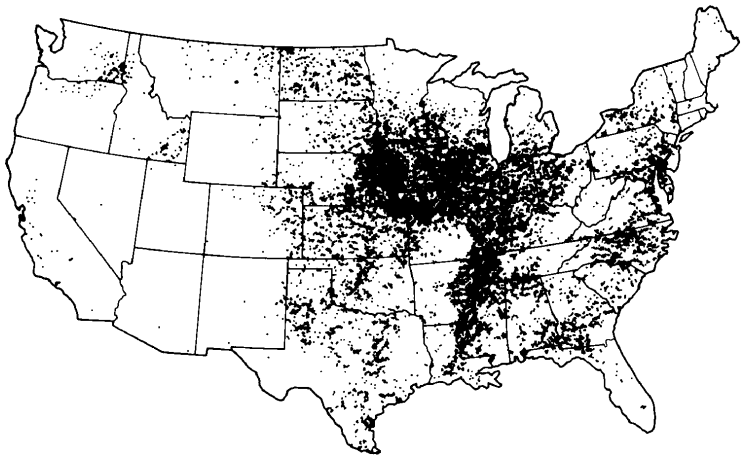


Figure 18.6 Pattern of soil erosion in the continental U.S. as of 1977. The dark areas indicate locations where the greatest erosion is occurring.

Wind erosion, such as occurs on the generally dry, high plains soils of eastern Colorado, poses another threat. After the Dust Bowl days of the 1930s, much of this land was allowed to revert to grassland, and the topsoil was held in place by the strong root systems of the grass cover. However, in an effort to grow more wheat and improve the sale value of the land, much of it was later returned to cultivation. For example, from 1979 through 1982, more than 450,000 acres of Colorado grasslands were plowed. Much of this was done by speculators who purchased grassland at a low price of $100–$200 per acre, broke it up, and sold it as cultivated land at more than double the original purchase price. Although freshly cultivated grassland may yield well for 1 or 2 years, the nutrients and soil moisture are rapidly exhausted and the land becomes very susceptible to wind erosion.

The preservation of soil from erosion is commonly termed **soil conservation**. There are a number of solutions to the soil erosion problem. Some are old, well-known agricultural practices such as terracing, contour plowing, and periodically planting fields with cover crops such as clover. For some crops, **no-till agriculture**, now commonly called **conservation tillage**, greatly reduces erosion. This practice consists of planting a crop among the residue of the previous year's crop without plowing. Weeds are killed in the newly planted crop row by application of a herbicide prior to planting. The surface residue of plant material left on top of the soil prevents erosion.

Another, more experimental, solution to the soil erosion problem is the cultivation of perennial plants that develop large root systems and come up each spring after being harvested the previous fall. For example, a perennial corn plant has been developed by crossing corn with a distant wild relative, teosinte, which grows in Central America. Unfortunately, the resulting plant does not give outstanding grain

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yields. It should be noted that an annual plant's ability to propagate depends upon producing large quantities of seeds, whereas a perennial plant must develop a strong root system with bulbous growths called rhizomes that store food for the coming year. However, it is possible that the application of genetic engineering (see Section 18.9) may result in the development of perennial crops with good seed yields. The cultivation of such a crop would cut down on a great deal of soil erosion.

The best known perennial plants are trees, which are very effective in stopping soil erosion. Wood from trees can be used as biomass fuel, as a source of raw materials, and as food (see below). There is a tremendous unrealized potential for an increase in the production of biomass from trees. For example, the production of biomass from natural forests of loblolly pine trees in South Carolina has been about three dry tons per hectare per year. This has now been increased at least fourfold through selection of superior trees, and 30 tons may eventually be possible. In Brazil, experiments were conducted with a species of eucalyptus, which has a seven-year growth cycle. With improved selection of trees, the annual yields for three successive cycles of these trees in dry tons per hectare per year were 23, 33, and 40.

The most important use for wood is, of course, as lumber for construction. This use will remain important as higher energy prices increase the costs of other construction materials such as steel, aluminum, and cement. Wood is about 50 percent cellulose, which can be hydrolyzed by rapidly improving enzyme processes to yield glucose sugar. The glucose can be used directly as food, fermented to ethyl alcohol for fuel (gasohol), or employed as a carbon and energy source for protein-producing yeasts. Given these and other potential uses, the future of trees as an environmentally desirable and profitable crop is very bright.

Soil and Water Resources

The conservation of soil and the protection of water resources are strongly interrelated. Most fresh water falls initially on soil, and the condition of the soil largely determines the fate of the water and how much is retained in a usable condition. The land area upon which rainwater falls is called a **watershed**. In addition to collecting the water, the watershed determines the direction and rate of flow and the degree of water infiltration into groundwater aquifers (see the hydrologic cycle in Figure 2.1). Excessive rates of water flow prevent infiltration, lead to flash floods, and cause soil erosion. Measures taken to enhance the utility of land as a watershed also fortunately help prevent erosion. Some of these measures involve modification of the contour of the soil, particularly terracing, construction of waterways, and construction of water-retaining ponds. Waterways are planted with grass to prevent erosion, and water-retaining crops and bands of trees can be planted on the contour to achieve much the same goal. Reforestation and control of damaging grazing practices conserve both soil and water.

18.10 GENETIC ENGINEERING AND AGRICULTURE

The nuclei of living cells contain the genetic instruction for cell reproduction. These instructions are in the form of a special material called deoxyribonucleic acid, DNA. In combination with proteins, DNA makes up the cell chromosomes. During

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the 1970s, the ability to manipulate DNA through genetic engineering became a reality, and during the 1980s, it became the basis of a major industry. The deliberate modification of genetic material falls into the category of recombinant DNA technology. Recombinant DNA gets its name from the fact that it contains DNA from two different organisms, recombined together. This technology promises some exciting developments in agriculture and, indeed, is expected to lead to a "second green revolution."

The first green revolution of the mid-1960s used conventional plant-breeding techniques of selective breeding, hybridization, cross-pollination, and back-crossing to develop new strains of rice, wheat, and corn which, when combined with chemical fertilizers, yielded spectacularly increased crop yields. For example, India's output of grain increased 50 %. By working at the cellular level, however, it is now possible to greatly accelerate the process of plant breeding. Thus, plants may be developed that resist particular diseases, grow in seawater, or have much higher productivity. The possibility exists for developing entirely new kinds of plants.

One exciting possibility with genetic engineering is the development of plants other than legumes that fix their own nitrogen. For example, if nitrogen-fixing corn could be developed, the savings in fertilizer would be enormous. Furthermore, since the nitrogen is fixed in an organic form in plant root structures, there would be no pollutant runoff of chemical fertilizers.

Another promising possibility with genetic engineering is increased efficiency of photosynthesis. Plants utilize only about one % of the sunlight striking their leaves, so there is appreciable room for improvement in that area.

Cell-culture techniques can be applied in which billions of cells are allowed to grow in a medium and develop mutants which, for example, might be resistant to particular viruses or herbicides or have other desirable qualities. If the cells with the desired qualities can be regenerated into whole plants, results can be obtained that might have taken decades using conventional plant-breeding techniques.

Despite the enormous potential of the green revolution, genetic engineering, and more intensive cultivation of land to produce food and fiber, these technologies cannot be relied upon to support an uncontrolled increase in world population, and may even simply postpone an inevitable day of reckoning with the consequences of population growth. Changes in climate resulting from global warming (greenhouse effect, Section 15.6), ozone depletion (by chlorofluorocarbons, Section 16.4), or natural disasters such as massive volcanic eruptions or collisions with large meteorites can, and almost certainly will, result in worldwide famine conditions in the future that no agricultural technology will be able to alleviate.

There has been strong resistance to transgenic crops and livestock in some quarters. This is especially true in Europe. Reports that pollen from transgenic corn producing an insecticide of bacterial origin has killed monarch butterfly caterpillars led the European Commission, the executive body of the the European Union, to suspend action on seven transgenic crops that it was considering for approval. The Commission had already approved 16 varieties of transgenic corn, potatoes, rape, sugar beets, turnips, and other crops. As of 1999, it appeared that major agricultural product processors in the U.S. would have to certify products as "GM free" (free of genetically modified products) for export to Europe.

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18.11 AGRICULTURE AND HEALTH

Some authorities hold that soil has an appreciable effect upon health. An obvious way in which such an effect might be manifested is the incorporation into food of micronutrient elements essential for human health. One such nutrient (which is toxic at overdose levels) is selenium. It is definitely known that the health of animals is adversely affected in selenium-deficient areas as it is in areas of selenium excess. Human health might be similarly affected.

There are some striking geographic correlations with the occurrence of cancer, some of which may be due to soil type. A high incidence of stomach cancer occurs in areas with certain types of soil in the Netherlands, the United States, France, Wales, and Scandinavia. These soils are high in organic matter content, are acidic, and are frequently waterlogged. A "stomach-cancer-prone lifestyle" has been described, which includes consumption of home-grown food, consumption of water from one's own well, and reliance on native and uncommon foodstuffs.

One possible reason for the existence of "stomach-cancer-producing soils" is the production of cancer-causing secondary metabolites by plants and microorganisms. Secondary metabolites are biochemical compounds that are of no apparent use to the organism producing them. It is believed that they are formed from the precursors of primary metabolites when the primary metabolites accumulate to excessive levels.

The role of soil in environmental health is not well known, nor has it been extensively studied. The amount of research on the influence of soil in producing foods that are more nutritious and lower in content of naturally occurring toxic substances is quite small compared to research on higher soil productivity. It is to be hoped that the environmental health aspects of soil and its products will receive much greater emphasis in the future.

Chemical Contamination

Human activities, most commonly pesticide application, may contaminate food grown on soil. An interesting example of such contamination occurred in Hawaii in early 1982. It was found that milk from several sources on Oahu contained very high levels of heptachlor (see Table 7.5). This pesticide causes cancer and liver disorders in mice; therefore, it is a suspected human carcinogen. Remarkably, in this case it was not until 57 days after the initial discovery that the public was informed of the contamination by the Department of Health. The source of heptachlor was traced to contaminated "green chop," chopped-up pineapple leaves fed to cattle. Although heptachlor was banned for most applications, Hawaiian pineapple growers had obtained special federal permission to use it to control mealybug wilt. Although it was specified that green chop could not be collected within one year of the last application of the pesticide, this regulation was apparently violated, and the result was distribution of contaminated milk to consumers.

In the late 1980s, Alar residues on food caused considerable controversy in the marketplace. **Alar**, daminozide, is a growth regulator that was widely used on apples to bring about uniform ripening of the fruit, and to improve the firmness and color of the apples. It was discontinued for this purpose after 1988 because of concerns that it might cause cancer, particularly in those children who consume relatively large amounts of apples, apple juice, and other apple products. Dire predictions were made

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in the industry of crop losses and financial devastation. However, the 1989 apple crop, which was the first without Alar in the U.S., had a value of $1.0 billion, only $0.1 billion less than that of the 1988 crop. Production of apples has continued since then without serious problems from the unavailability of Alar.

A possible source of soil contamination results from recycling industrial wastes for fertilizer. According to data compiled by the Environmental Working Group (EWG) during the 1990s, approximately 25 million kg per year of potentially toxic wastes were used to prepare fertilizers that contained elevated levels of arsenic, cadmium, lead, radioactive materials, and dioxins. A potential source of heavy metal pollution in fertilizers is ash from furnaces used to recycle steel, commonly processed to provide zinc in zinc-deficient soils.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Agriculture, defined as [1]_____ _____, can be divided into the two main categories of [2]_____ _____. The crops that provide for most of human caloric food intake, as well as much food for animals, are [3]_____. Soil can be defined as [4]_____ _____ formed by [5]_____ _____. Soils exhibit distinctive layers with increasing depth called [6]_____, the top one of which is called the A horizon or [7]_____.Transpiration is a process in which [8] _____. In addition to solid mineral and organic matter and water, roughly 35% of the volume of typical soil is composed of [9]_____. Most of soil organic matter is composed of [10]_____, which consists of a base-soluble fraction called [11]_____ _____ and an insoluble fraction called [12]_____. The soil solution serves to [13]_____ _____ _____. An important property of soil abbreviated CED expresses its capacity to [14]_____. The reaction,

$$\text{Soil}\}Ca^{2+} + 2CO_2 + 2H_2O \rightarrow \text{Soil}\}(H^+)_2 + Ca^{2+}(\text{root}) + 2HCO_3^-$$

shows why soil had a tendency to become [15]_____. The reaction,

$$\text{Soil}\}(H^+)_2 + CaCO_3 \rightarrow \text{Soil}\}Ca^{2+} + CO_2 + H_2O$$

shows [16]_____. The macronutrients often lacking in soil and commonly added as fertilizer are [17]_____

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_____. Sulfur is assimilated by plants as [18]_____ _____. In most soils, over [19]_____ of the nitrogen content is organic, primarily the product of [20]_____ _____. Legumes are plants that host bacteria on their roots capable of [21]_____. Essential plant micronutrients include [22]_____ _____. Phytoremediation uses the growth of plants to [23]_____. The numbers in a notation for fertilizer such as 8-13-8 refers to, respectively, _____ _____. The [24]_____ of soil is particularly important with respect to biodegradation of wastes. Desertification refers to the process associated with [25]_____ by which soil becomes [26]_____ _____. Soil erosion can occur by the action of both [27]_____. The preservation of soil from erosion is commonly termed [28], now commonly accomplished by the practice of [29]_____ _____. The land area upon which rainwater falls is called a [30]_____. Genetic engineering involves maniupulation of cellular [31]_____. The first "green revolution" of the mid-1960s used [32]_____ _____. Two promising possibilities with genetic engineering of plants, one of which would decrease the need for chemical fertilizers are [33]_____ _____. Food products certified to be "GM free" are those that are [34]_____ _____.

Answers to Chapter Summary

1. the production of food by growing crops and livestock
2. crop farming and livestock farming
3. cereals
4. a finely divided layer of weathered minerals and organic matter upon which plants grow
5. the weathering of parent rocks as the result of interactive geological, hydrological, and biological processes
6. horizons
7. topsoil
8. water enters the atmosphere from the plant's leaves
9. air-filled pores
10. humus
11. humic and fulvic acids
12. humin
13. transport chemical species to and from soil particles and provide intimate contact between the solutes and the soil particles
14. exchange cations
15. acidic

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16. treatment of excessively acidic soil
17. nitrogen, phosphorus, and potassium
18. the sulfate ion, SO_4^{2-}
19. 90%
20. the biodegradation of dead plants and animals
21. fixing nitrogen
22. boron, chlorine, copper, iron, manganese, molybdenum, and zinc
23. remove pollutants from ground
24. rhizosphere
25. drought and loss of fertility
26. unable to grow significant amounts of plant life
27. water and wind
28. soil conservation
29. no-till agriculture or conservation tillage
30. watershed
31. DNA
32. conventional plant-breeding techniques
33. ability of non-legume plants to fix N and increased efficiency of photosynthesis
34. free of genetically modified products

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QUESTIONS AND PROBLEMS

1. Give two examples of reactions involving manganese and iron compounds that might occur in waterlogged soil.

2. What temperature and moisture conditions favor the buildup of organic matter in

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soil?

3. "Cat clays" are soils containing a high level of iron pyrite, FeS_2. Hydrogen peroxide, H_2O_2, is added to such a soil, producing sulfate as a test for cat clays. Suggest the chemical reaction involved in this test.
4. What effect upon soil acidity would result from heavy fertilization with ammonium nitrate accompanied by exposure of the soil to air and the action of aerobic bacteria?
5. How many moles of H^+ ion are consumed when 200 kilograms of $NaNO_3$ undergo denitrification in soil?
6. What is the primary mechanism by which organic material in soil exchanges cations?
7. Prolonged waterlogging of soil does **not** (a) increase NO_3^- production, (b) increase Mn^{2+} concentration, (c) increase Fe^{2+} concentration, (d) have harmful effects upon most plants, (e) increase production of NH_4^+ from NO_3^-.
8. Of the following phenomena, the one that eventually makes soil more basic is (a) removal of metal cations by roots, (b) leaching of soil with CO_2-saturated water, (c) oxidation of soil pyrite, (d) fertilization with $(NH_4)_2SO_4$, (e) fertilization with KNO_3.
9. How many metric tons of farm manure are equivalent to 100 kg of 10-5-10 fertilizer?
10. How are the chelating agents that are produced from soil microorganisms involved in soil formation?
11. What specific compound is both a particular animal waste product and a major fertilizer?
12. What happens to the nitrogen/carbon ratio as organic matter degrades in soil?
13. To prepare a rich potting soil, a greenhouse operator mixed 75% "normal" soil with 25% peat. Estimate the cation-exchange capacity in milliequivalents/100 g of the product.
14. Explain why plants grown on either excessively acidic or excessively basic soils may suffer from calcium deficiency.
15. What are two mechanisms by which anions may be held by soil mineral matter?
16. Match the soil or soil-solution constituent in the left column with the soil condition described on the right, below:

A. High Mn^{2+} content in soil solution	1. "Cat clays" containing initially high levels of pyrite, FeS_2
B. Excess H^+	2. Soil in which biodegradation has not occurred to a great extent
C. High H^+ and SO_4^{2-} content	3. Waterlogged soil
D. High organic content	4. Soil, the fertility of which can be improved by

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adding limestone.

17. What are the three major ways in which pesticides are degraded in or on soil?
18. Lime from lead mine tailings containing 0.5% lead was applied at a rate of 10 metric tons per acre of soil and worked in to a depth of 20 cm. The soil density was 2.0 g/cm. To what extent did this add to the burden of lead in the soil? There are 640 acres per square mile and 1,609 meters per mile.
19. What are the processes occurring in soil that operate to reduce the harmful effects of pollutants?
20. Under what conditions do the reactions,

 $MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$

 and

 $Fe_2O_3 + 6H^+ + 2e^- \rightarrow 2Fe^{2+} + 3H_2O$

 occur in soil? Name two detrimental effects that can result from these reactions.
21. What are four important effects of organic matter in soil?
22. How might irrigation water treated with fertilizer containing potassium and ammonia become depleted of these nutrients in passing through humus-rich soil?
23. Match the following:

A. Subsoil	1. Weathered parent rocks from which the soil originated
B. Gravels	2. Largest particle size fraction (2–60 mm) according to the United Classification System
C. Topsoil	3. B horizon of soil
D. C horizon	4. Layer of maximum biological activity in soil that contains most of the soil organic matter

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Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC, 2001

19 INDUSTRIAL ECOLOGY AND ENVIRONMENTAL CHEMISTRY

19.1 INTRODUCTION AND HISTORY

At the beginning of Chapter 11, mention was made of the **anthrosphere** consisting of the things humans construct, use, and do in the environment. The anthrosphere constitutes a fifth sphere of the environment, along with the geosphere, hydrosphere, atmosphere, and biosphere. Any intelligent effort to maintain and enhance environmental quality must consider the anthrosphere along with these other four spheres. This chapter is devoted primarily to the anthrosphere. In so doing, it emphasizes the emerging science of industrial ecology, defined and explained below.

Industrial ecology *is an approach based upon systems engineering and ecological principles that integrates the production and consumption aspects of the design, production, use, and termination (decommissioning) of products and services in a manner that minimizes environmental impact while optimizing utilization of resources, energy, and capital*. The practice of industrial ecology represents an environmentally acceptable, sustainable means of providing goods and services. It is closely tied with environmental chemistry, and the two sciences work synergistically with each other.

Industrial ecology works within a system of industrial ecosystems, which mimic natural ecosystems. Natural ecosystems, usually driven by solar energy and photosynthesis, consist of an assembly of mutually interacting organisms and their environment, in which materials are interchanged in a largely cyclical manner. An ideal system of industrial ecology follows the flow of energy and materials through several levels, uses wastes from one part of the system as raw material for another part, and maximizes the efficiency of energy utilization. Whereas wastes, effluents, and products used to be regarded as leaving an industrial system at the point where a product or service was sold to a consumer, industrial ecology regards such materials as part of a larger system that must be considered until a complete cycle of manufacture, use, and disposal is completed.

From the discussion above and in the remainder of this book, it can be concluded

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that industrial ecology is all about *cyclization of materials*. This approach is summarized in a statement attributed to Kumar Patel of the University of California at Los Angles, "The goal is *cradle to reincarnation*, since if one is practicing industrial ecology correctly there is no grave." For the practice of industrial ecology to be as efficient as possible, cyclization of materials should occur at the highest possible level of material purity and stage of product development. As just one of many examples that could be cited, consider that it is much more efficient in terms of materials, energy, and monetary costs to bond a new rubber tread to a large, expensive tire used on heavy earth moving equipment than it is to try to separate the rubber from the tire and remold it into a new one.

The basis of industrial ecology is provided by the phenomenon of **industrial metabolism**, which refers to the ways in which an industrial system handles materials and energy, extracting needed materials from sources such as ores, using energy to assemble materials in desired ways, and disassembling materials and components. In this respect, an industrial ecosystem operates in a manner analogous to biological organisms, which act on biomolecules to perform anabolism (synthesis) and catabolism (degradation).

Just as occurs with biological systems, industrial enterprises can be assembled into **industrial ecosystems**. Such systems consist of a number (preferably large and diverse) of industrial enterprises acting synergistically and, for the most part, with each utilizing products and potential wastes from other members of the system. Such systems are best assembled through natural selection and, to a greater or lesser extent, such selection has occurred throughout the world. However, recognition of the existence and desirability of smoothly functioning industrial ecosystems can provide the basis for laws and regulations (or the repeal thereof) that give impetus to the establishment and efficient operation of such systems.

The term **sustainable development** has been used to describe industrial development that can be sustained without environmental damage and to the benefit of all people. Clearly, if humankind is to survive with a reasonable standard of living, something like "sustainable development" must evolve in which use of nonrenewable resources is minimized insofar as possible, and the capability to produce renewable resources (for example, by promoting soil conservation to maintain the capacity to grow biomass) is enhanced. This will require significant behavioral changes, particularly in limiting population growth and curbing humankind's appetite for increasing consumption of goods and energy.

19.2 INDUSTRIAL ECOSYSTEMS

A group of firms that practice industrial ecology through a system of industrial metabolism that is efficient in the use of both materials and resources constitute a functional **industrial ecosystem**. Such a system can be defined as a regional cluster of industrial firms and other entities linked together in a manner that enables them to utilize byproducts, materials, and energy between various enterprises in a mutually advantageous manner.

Figure 19.1 shows the main attributes of a functional industrial ecosystem, which, in the simplest sense, processes materials powered by a relatively abundant source of energy. Materials enter the system from a raw materials source and are put in a

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usable form by a primary materials producer. From there the materials go into manufacturing goods for consumers. Associated with various sectors of the operation are waste processors that can take byproduct materials, upgrade them, and feed them back into the system. An efficient, functional transportation system is required for the system to work well, and good communications links must exist among the various sectors. A key material in the system is water, and it is often in limited supply in highly populated arid regions of the world.

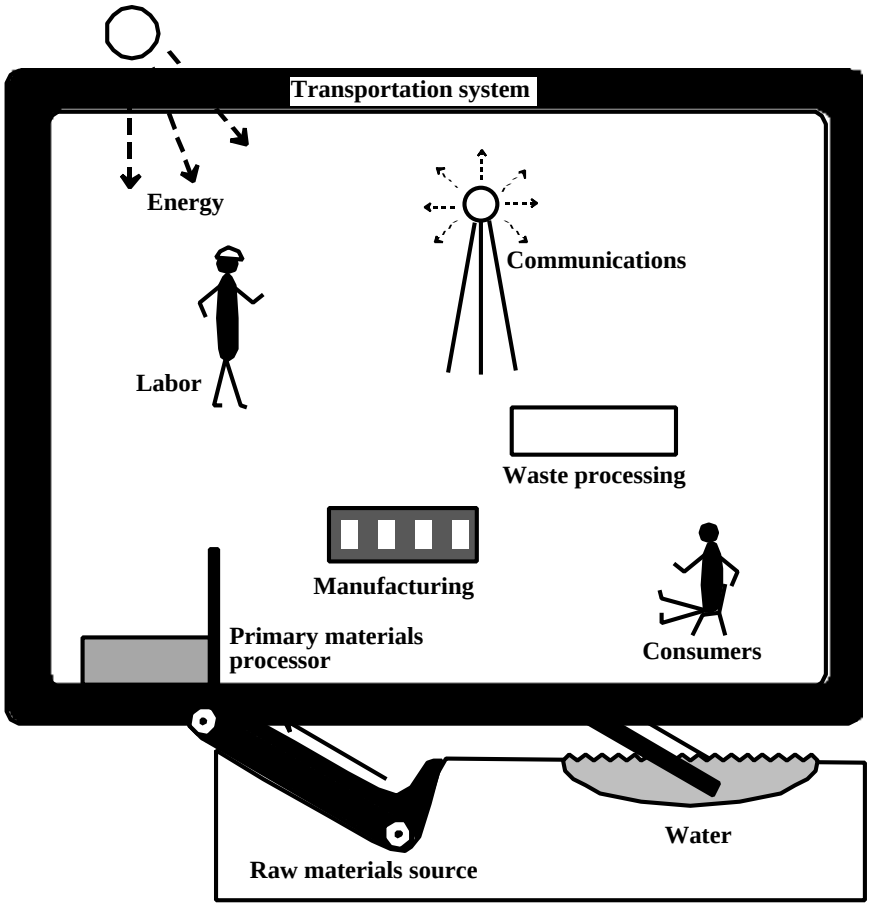


Figure 19.1 Major components required for an industrial system. When these components exist symbiotically, utilizing waste materials from one concern as feedstock for another, they compose a functioning industrial ecosystem.

A successfully operating industrial ecosystem provides several benefits. Such a system *reduces pollution*. It results in *high energy efficiency* compared to systems of firms that are not linked and it *reduces consumption of virgin materials* because it *maximizes materials recycle. Reduction of amounts of wastes* is another advantage of a functional system of industrial ecology. Finally, a key measure of the success of a system of industrial ecology is *increased market value of products* relative to material and energy consumption.

An industrial ecosystem can be set up using two basic complementary

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approaches. Within an industry, emphasis may be placed upon product durability and amenability to repair and recycle, which are compatible with the practice of industrial ecology. Instead of selling products, a concern may emphasize leasing so that it can facilitate recycling. The second approach emphasizes interactions between concerns so that they operate in keeping with good practice of industrial ecology. This approach facilitates materials and energy flow, exchange, and recycle between various firms in the industrial ecosystem.

An important aspect of an industrial ecosystem is the practice of a high degree of **industrial symbiosis**. Symbiotic relationships in natural biological systems occur when two often very dissimilar organisms live together in a mutually advantageous manner. Analogous symbiotic relationships in which firms utilize each other's residual materials form the basis of relationships between firms in a functional industrial ecosystem. Examples of industrial symbiosis are cited in Section 19.14 in the discussion of the Kalundborg, Denmark, industrial ecosystem.

A useful way to view an industrial ecosystem is geographically, often on the basis of a transportation network. An example is the Houston Ship Channel, which stretches for many kilometers and is bordered by a large number of petrochemical concerns that exist to mutual advantage through the exchange of materials and energy. The purification of natural gas by concerns located along the channel yields lower molecular mass hydrocarbons such as ethane and propane that can be used by other concerns, for example, in polymers manufacture. Sulfur removed from natural gas and petroleum can be used to manufacture sulfuric acid, which in turn is a key raw material for the manufacture of a number of other chemicals.

19.3 THE FIVE MAJOR COMPONENTS OF AN INDUSTRIAL ECOSYSTEM

Industrial ecosystems can be broadly defined to include all types of production, processing, and consumption. These include, for example, agricultural production as well as purely industrial operations. It is useful to define five major components of an industrial ecosystem, as shown in Figure 19.2. These are (1) a primary materials producer, (2) a source or sources of energy, (3) a materials processing and manufacturing sector, (4) a waste-processing sector, and (5) a consumer sector. In such an idealized system, the flow of materials among the four major hubs is very high. Each constituent of the system evolves in a manner that maximizes the efficiency with which the system utilizes materials and energy.

Primary Materials and Energy Producers

It is convenient to consider the primary materials producers and the energy generators together because both materials and energy are required for the industrial ecosystem to operate. The primary materials producer or producers may consist of one or several enterprises devoted to providing the basic materials that sustain the industrial ecosystem. Most generally, in any realistic industrial ecosystem a significant fraction of the material processed by the system consists of virgin materials. In a number of cases, and increasingly so as pressures build to recycle materials, significant amounts of the materials come from recycling sources.

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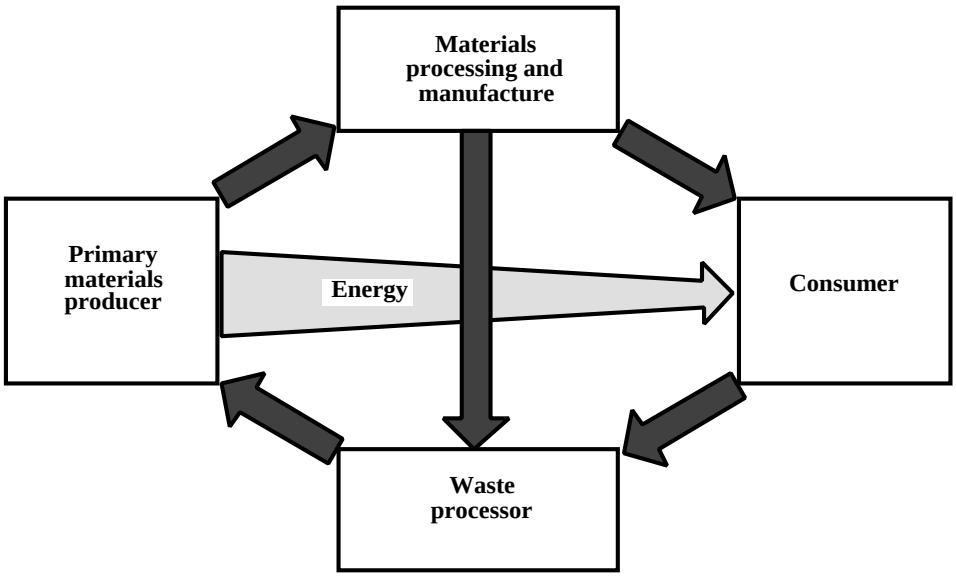


Figure 19.2 The major constituents or "hubs" of an industrial ecosystem.

The processes that virgin materials entering the system are subjected to vary with the kind of material, but can generally be divided into several major steps. Typically, the first step is **extraction**, designed to remove the desired substance as completely as possible from the other substances with which it occurs. This stage of materials processing can produce large quantities of waste material requiring disposal, as is the case with some metal ores in which the metal makes up a small percentage of the ore that is mined. In other cases, such as corn grain providing the basis of a corn products industry, the "waste,"—in this specific example the cornstalks associated with the grain—can be left in place (cornstalks returned to soil serve to add humus and improve soil quality). A **concentration** step may follow extraction to put the desired material into a purer form. After concentration, the material may be put through additional **refining** steps that may involve **separations**. Following these steps, the material is usually subjected to additional **processing** and **preparation** leading to the finished materials. Throughout the various steps of extraction, concentration, separation, refining, processing, preparation, and finishing, various physical and chemical operations are used, and wastes requiring disposal may be produced. Recycled materials may be introduced at various parts of the process, although they are usually introduced into the system following the concentration step.

The extraction and preparation of energy sources can follow many of the steps outlined above for the extraction and preparation of materials. For example, the processes involved in extracting uranium from ore, enriching it in the fissionable uranium-235 isotope, and casting it into fuel rods for nuclear fission power production include all of those outlined above for materials. On the other hand, some rich sources of coal are essentially scooped from a coal seam and sent to a power plant for power generation with only minimal processing, such as sorting and grinding.

Recycled materials added to the system at the primary materials and energy production phase may be from both pre- and postconsumer sources. As examples,

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recycled paper may be macerated and added at the pulping stage of paper manufacture. Recycled aluminum may be added at the molten metal stage of aluminum metal production.

Materials Processing and Manufacturing Sector

Finished materials from primary materials producers are fabricated to make products in the materials processing and manufacturing sector. This sector is often a very complex system. For example, the manufacture of an automobile requires steel for the frame, plastic for various components, rubber in tires, lead in the battery, copper in the wiring, and cloth or leather for the seats, along with a large number of other materials. Typically, the first step in materials manufacturing and processing is a forming operation. For example, sheet steel suitable for making automobile frames may be cut, pressed, and welded into the configuration needed to make a frame. At this step, some wastes may be produced that require disposal. An example of such wastes consists of carbon fiber/epoxy composites left over from forming parts such as jet aircraft engine housings. Finished components from the forming step are fabricated into finished products that are ready for the consumer market.

The materials processing and manufacturing sector presents several opportunities for recycling. At this point, it might be useful to define two different streams of recycled materials:

- **Process recycle streams** consisting of materials recycled in the manufacturing operation itself
- **External recycle streams** consisting of materials recycled from other manufacturers or from postconsumer products

Materials suitable for recycling can vary significantly. Generally, materials from the process recycle streams are quite suitable for recycling because they are the same materials used in the manufacturing operation. Recycled materials from the outside, especially those from postconsumer sources, may be quite variable in their characteristics because of the lack of effective controls over recycled postconsumer materials. Therefore, manufacturers may be reluctant to use such substances.

The Consumer Sector

In the consumer sector, products are sold or leased to the consumers who use them. The duration and intensity of use vary widely with the product; paper towels are used only once, whereas an automobile may be used thousands of times over many years. In all cases, however, the end of the useful lifetime of the product is reached and it is either (1) discarded or (2) recycled. The success of a total industrial ecology system can be measured largely by the degree to which recycling predominates over disposal.

Waste Processing Sector

Recycling has become so widely practiced that an entirely separate waste processing sector of an economic system can now be defined consisting of enterprises

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that deal specifically with the collection, separation, and processing of recyclable materials and their distribution to end users. Such operations may be entirely private or they may involve cooperative efforts with governmental sectors. They are often driven by laws and regulations as well as positive economic and regulatory incentives for their recycle.

19.4 INDUSTRIAL METABOLISM

Industrial metabolism in its entirety follows the flows of materials and energy from their initial sources through an industrial system, to the consumer, and to their ultimate disposal. In biological systems, metabolism can be studied at any level ranging from the molecular processes that occur in individual cells through the multiple processes and metabolic cycles that occur in individual organs, and to the overall process of metabolism that takes place in the whole organism. Similarly, industrial metabolism can be examined as individual unit operations within an industrial operation, at the factory level, at the industry level, and globally. For an industrial ecology approach, it is often most useful to view industrial metabolic processes at the regional level, large enough to have a number of industries with a variety of potential waste products that might be used by other industries, but small enough to permit transport and exchange of materials among various industries. To minimize pollution, it can be useful to consider units consisting of environmental domains, such as atmospheric basins or watersheds.

Unlike the living metabolic processes that occur in natural systems where true waste products are very rare, industrial metabolism as it is now practiced has a vexing tendency to dilute, degrade, and disperse materials to an extent that they are no longer useful but are still harmful to the environment. Indeed, waste has been defined as *dissipative use of natural resources*. In addition to simple loss from dilution and dispersion in the environment, materials may be lost by being tied up in low-energy forms or by being put into a chemical form from which they are very difficult to be retrieved.

An example of dissipation of material resulting in environmental pollution, now a very much diminished problem, was the widespread use of lead in tetraethyl lead antiknock additive in gasoline. The net result of this use was to disperse lead throughout the environment in auto exhaust gas, with no hope of recovery.

Industrial Metabolism and Biological Analogies

The strong analogy between natural ecosystems and efficient industrial systems was first clearly stated in 1989 by Frosch and Gallopoulos in an article in *Scientific American* cited under Supplementary References. A natural ecosystem, which is usually driven by solar energy and photosynthesis, consists of an assembly of mutually interacting organisms and their environment in which materials are interchanged in a largely cyclical manner. It is possible to visualize an analogous industrial ecosystem in which materials are cycled, driven by an energy source.

It is useful to view the metabolic processes of a natural ecosystem as a whole, rather than just observing each individual organism. Like a natural ecosystem, an industrial ecosystem synthesizes substances, thus performing anabolism, and it degrades substances, thereby performing in a manner analogous to biological

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catabolism. Typically, a large amount of a material, such as an ore or petroleum source, is metabolized to yield a relatively small quantity of a finished product. The objective of a properly designed and operated industrial ecosystem is to perform industrial metabolism in the most efficient manner possible so that the least possible raw material is used, the maximum amounts of materials are recycled through the system, and the most efficient possible use is made of the energy that sustains the industrial ecosystem.

An ideal biological ecosystem involves many organisms living in harmony with their environment without any net consumption of resources or production of waste products. The only input required for such an ecosystem is solar energy. This energy is captured and used by photosynthetic primary producers to convert carbon dioxide, water, and other inorganic materials into biomass. Herbivores ingest this biomass and use it for their energy and to synthesize their own biomass. Carnivores, of which there may be several levels, consume herbivores, and a food chain exists that may consist of several levels of organisms. Parasites exist on or in other organisms. Saprophytes and bacteria and fungi responsible for decay utilize and degrade biomass, eventually converting it back to simple inorganic constituents through the process of mineralization. Symbiotic and synergistic relationships abound in a natural ecosystem. Thus, an ideal ecosystem exists indefinitely in a steady-state condition without causing any net degradation of its environment.

A natural ecosystem can be visualized as having compartments in which various *stocks* of materials are kept, connected by *flows* of materials. Examples of such compartments include soil, which is a repository of plant nutrients; a body of water, such as a lake; and the atmosphere, which is a repository of carbon dioxide required for photosynthesis. In an undisturbed natural ecosystem, the quantities of the materials in each of these compartments remains relatively stable because such systems are inherently recycling. In contrast, the quantities of materials in the compartments of an industrial system are not constant. Reservoirs of raw materials, such as essential minerals, are constantly diminishing, although with new discoveries of mineral resources, they might *appear* to increase. Furthermore, reservoirs of wastes in an industrial system continually increase as materials traverse an essentially one-way path through the system. Sustainable industrial systems maximize recycling so that quantities of materials in the reservoirs remain constant as much as possible.

Systems of biological metabolism are **self-regulating**. At the level of the individual organism, regulation is accomplished internally by biological regulatory mechanisms, such as those that employ hormones. At the ecosystem level, regulation occurs through competition among organisms for available resources. In a manner analogous to natural ecosystems, industrial systems can be designed in principle to operate in a similar steady-state manner, ideally neither consuming nonrenewable resources nor producing useless waste products. Such systems can be self-regulating, with the economic system operating under the laws of supply and demand as the regulatory mechanism.

A comparison of the metabolisms of natural ecosystems with that of industrial systems as they are commonly encountered shows a marked contrast. These contrasts are highlighted in Table 19.1.

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Table 19.1 Metabolic Characteristics of Natural Ecosystems and Industrial Systems

Characteristic	Natural ecosystems	Current industrial systems
Basic unit	Organism	Firm
Material pathways	Closed loops	Largely one-way
Recycling	Essentially complete	Often very low
Material fate	Tend to concentrate, such as atmospheric CO_2 converted to biomass by photosynthesis	Dissipative to produce materials too dilute to use, but concentrated enough to pollute
Reproduction	A major function of organisms is reproduction	Production of goods and services is the prime objective, not reproduction per se

Attractive as the idea may sound; in a modern society and especially in a "global economy," a complete industrial ecosystem carrying out industrial metabolism in an idealized fashion is not practical or even desirable. Essentially all modern communities produce at least one product that is exported to the outside, and must bring in materials and energy sources from elsewhere. A more realistic model of an industrial ecosystem is one in which raw materials are imported from the outside and at least one major product is exported from the system, but in which a number of enterprises coexist synergistically, utilizing each other's products and services to mutual advantage. In such a system, typically, raw materials flow into a primary raw material processor, which converts them to a processed material. The processed material then goes to one or more fabricators that make a product for distribution and sale. Associated with the enterprise as a whole are suppliers of a variety of materials, items, or services, and processors of secondary materials or wastes. To meet the criteria of an industrial ecosystem, as many of the byproducts and wastes as possible must be utilized and processed within the system.

Although industrial systems are self-regulating, they are not necessarily so in a manner conducive to sustainability; indeed, the opposite is frequently the case. Left to their own devices and operating under the principles of traditional economics, industrial systems tend toward a state of equilibrium or maximum entropy in which essential materials have been exploited, run through the system, and dissipated to the environment in dilute, useless, sometimes harmful forms. A central question is, therefore, the time scale on which this irreversible dissipation is allowed to occur. If it is a few decades, modern civilization is in real trouble; if it is on a scale of thousands of years, there is ample time to take corrective action to maintain sustainability. A challenge to modern industrialized societies is to modify industrial systems to maximize the time spans under which sustainability may be achieved.

19.5 LEVELS OF MATERIALS UTILIZATION

There are two extremes in levels of materials utilization in industrial systems. At

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the most inefficient level, as shown in Figure 19.3, raw materials are viewed as being unlimited and no consideration is given to limiting wastes. Such an approach was typical of industrial development in the U.S. in the 1800s and early 1900s when the prevailing view was that there were no limits to ores, fossil energy resources, and other kinds of raw materials; furthermore, it was generally held that the continent had an unlimited capacity to absorb industrial wastes.

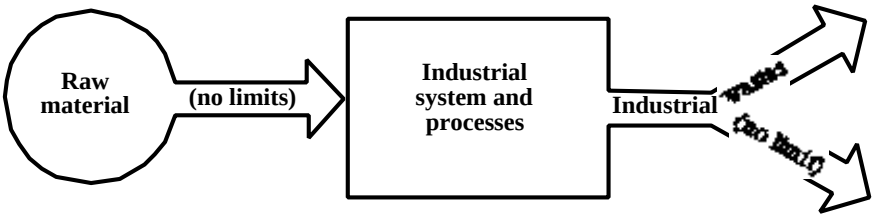


Figure 19.3 An industrial system without limits on either raw materials consumed or wastes produced.

A second kind of industrial system in which both raw materials and wastes are limited to greater or lesser extents is illustrated in Figure 19.4. Such a system has a relatively large circulation of materials within the industrial system as a whole, compared with reduced quantities of material going into the system and relatively lower production of wastes. Such systems are typical of those in industrialized nations and modern economic systems in which shortages of raw materials and limits to the places to put wastes are beginning to be felt. Even with such constraints, large quantities of materials are extracted, processed, and used, then either disposed of in the environment in concentrated form (hazardous wastes) or dispersed. In recent years, regulations and other constraints have markedly decreased point source pollution from industrial activity. However, because of the sheer volume of materials processed through industrial societies, dissipative pollution continues to be a problem.

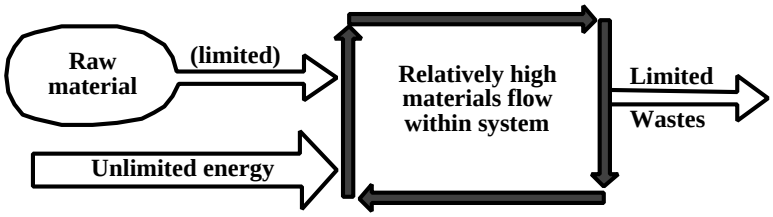


Figure 19.4 Illustration of an industrial system in which both the utilization of raw materials and the production of wastes are limited to a certain degree.

An industrial ecosystem with no materials input and no wastes is illustrated in Figure 19.5. The material flows within the system itself are quite high. In addition, the energy requirements of such a system can be rather high, and a key to its successful operation is often an abundant, minimally polluting primary source of energy. Such a system is an idealized one that can never be realized in practice, but it serves as a useful goal around which more-practical and achievable systems can be based.

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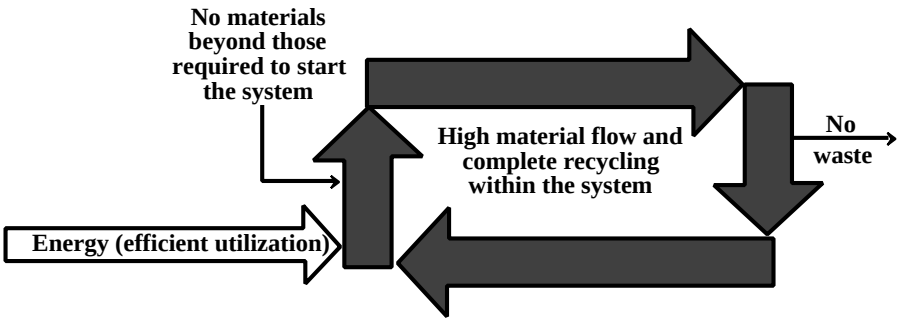


Figure 19.5 Idealized industrial ecosystem in which no materials are required for input beyond those needed to start the system. Energy requirements are relatively high, and the material flow within the system is high and continuous.

19.6 LINKS TO OTHER ENVIRONMENTAL SPHERES

Having addressed industrial ecology largely from the anthrospheric viewpoint, it is now appropriate to consider how the anthrosphere and the practice of indus-rial ecology influence the other four spheres of the environment—the atmosphere, the hydrosphere, the geosphere, and the biosphere. Influences of industrial activities, broadly defined to include energy and agricultural production as well as manufacture of goods and provision of essential services, can range from minor effects all the way up to major perturbations of the environment that may pose significant threats to Earth's ability to support life. Such influences can range from highly localized ones occurring for only a brief period of time to global effects that have the potential to last for centuries. An example of the former would be an isolated incident of water pollution by oxygen-consuming organic matter in a reservoir. The damage is often confined to the reservoir and only for the relatively short period of time required to degrade the wastes and replenish the oxygen supply. The prime example of a long-term global effect is the emission of greenhouse gases, which has the potential to change Earth's entire climate for thousands of years. An effect of intermediate duration is contamination of the atmosphere with ozone-destroying chlorofluorocarbons (Chapter 16, Section 16.4), an effect that will last for several decades after release of these substances has been stopped.

The major goal of industrial ecology, therefore, must be to minimize or eliminate detrimental effects of anthrospheric activities on other spheres of the environment. Beyond environmental preservation, the practice of industrial ecology should also improve and enhance environmental conditions. Listed below are the major anthrospheric activities along with their potential effects on other environmental spheres.

Fossil fuel combustion

Atmosphere: The greatest potential effect is greenhouse warming. Emission of partially combusted hydrocarbons and nitrogen oxides can cause formation of photochemical oxidants (photochemical smog). Acid precipitation may be caused by emissions of sulfur oxides from fuel combustion. General deterioration of atmospheric

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quality may occur through reduced visibility.

Hydrosphere: The potential exists for water pollution from acid mine water, petroleum production by-product brines, acid precipitation, and heating of water used to cool power plants.

Geosphere: The greatest potential effects are disturbance of land from coal mining.

Biosphere: Most effects are indirect as the result of influences on the atmosphere, hydrosphere, and geosphere.

Industrial manufacturing and processing

Atmosphere: Greatest potential effects are due to emissions of gases, vapors, and particles. These include greenhouse gases, acid gases, particles, precursors to photochemical smog formation, and species with the potential to deplete stratospheric ozone.

Hydrosphere: Industrial activities can contaminate water with a variety of pollutants. Consumptive uses of water may put pressure on limited water supplies, especially in arid regions. Water used for cooling may be thermally polluted.

Geosphere: The greatest effect results from the extractive industries through which minerals are recovered. The geosphere may be contaminated by solid and hazardous wastes, and available landfill space may become depleted.

Biosphere: The greatest direct effect is from the distribution of toxic substances as the result of industrial activities. There may also be significant indirect effects resulting from deterioration of the atmosphere, hydrosphere, and geosphere.

Crop production

Atmosphere: A major potential effect is emission of greenhouse gases as the result of deforestation and "slash and burn" agriculture to grow more crops. Significant amounts of greenhouse gas methane are emitted into the atmosphere as the result of methane-generating bacteria growing in rice paddies.

Hydrosphere: Large quantities of water are used for irrigation. Some of the water is lost by transpiration from plants, and some by infiltration to groundwater. Water returned to the hydrosphere from irrigation may have an excessively high salinity. Surface water and groundwater may become contaminated by solids, fertilizers, and herbicides from crop production.

Geosphere: Large areas of the geosphere may be disturbed by cultivation to produce crops. Topsoil can be lost from water and wind erosion. Proper agricultural practices, such as contour farming and low-tillage agriculture, minimize these effects and might even enhance soil quality.

Biosphere: Organisms are profoundly affected by agricultural practices designed to produce crops. Entire ecosystems are destroyed and replaced by other

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"anthrospheric" ecosystems. The greatest effect on the biosphere is loss of species diversity from the destruction of natural ecosystems, and from the cultivation of only limited strains of crops.

Livestock production (domestic animals)

Atmosphere: Ruminant animals are significant producers of greenhouse gas methane as the result of methane-producing bacteria in their digestive systems.

Hydrosphere: Livestock production requires large quantities of water. Large amounts of oxygen-consuming wastes that might contaminate surface water are produced by livestock. Nitrogen wastes from the manure and urine of animals in feedlots may cause nitrate contamination of groundwater.

Geosphere: The production of a unit mass of food from livestock sources requires much more crop production than is required for grains consumed directly by humans. A major impetus behind destruction of rain forests has been to grow forage and other foods for livestock. Rangeland has deteriorated because of overgrazing.

Biosphere: A major effect is loss of species diversity. This occurs even within domestic strains of livestock where modern breeding practices have resulted in the loss of entire breeds of livestock. The ultimate loss of domestic diversity occurs when animals are cloned.

The most environmentally damaging effects of human activities are those that are cumulative. As noted previously, the most significant of these at present is likely the accumulation of greenhouse gases that have the potential to cause global warming. Some environmental problems, such as those resulting from the emission of photochemical smog-forming pollutants into the atmosphere are potentially reversible. However, by the time global warming has been demonstrated to be a genuine problem, if such turns out to be the case, the damage will have been done, and little, if anything, will be able to reverse it.

19.7 CONSIDERATION OF ENVIRONMENTAL IMPACTS IN INDUSTRIAL ECOLOGY

By its nature, industrial production has an impact upon the environment. Whenever raw materials are extracted, processed, used, and eventually discarded, some environmental impacts will occur. In designing an industrial ecological system, several major kinds of environmental impacts must be considered in order to minimize them and keep them within acceptable limits. These impacts and the measures taken to alleviate them are discussed below.

For most industrial processes, the first environmental impact is that of extracting raw materials. This can be a straightforward case of mineral extraction, or it can be less direct, such as utilization of biomass grown on forest or crop land. A basic decision, therefore, is the choice of the kind of material to be used. Wherever possible, materials should be chosen that are not likely to be in short supply in the foreseeable future. As an example, the silica used to make the lines employed for fiber-optics communication is in unlimited supply and a much better choice for communication

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lines than copper wire made from limited supplies of copper ore.

Industrial ecology systems should be designed to reduce or even totally eliminate air pollutant emissions. Among the most notable recent progress in that area has been the marked reduction and even total elimination of solvent vapor emissions (volatile organic carbon, VOC), particularly those from organochlorine solvents. Some progress in this area has been made with more-effective trapping of solvent vapors. In other cases, the use of the solvents has been totally eliminated. This is the case for chlorofluorocarbons (CFCs), which are no longer used in plastic foam blowing and parts cleaning because of their potential to affect stratospheric ozone. Other air pollutant emissions that should be eliminated are hydrocarbon vapors, including those of methane, CH_4, and oxides of nitrogen or sulfur.

Discharges of water pollutants should be entirely eliminated wherever possible. For many decades, efficient and effective water treatment systems have been employed that minimize water pollution. However, these are "end of pipe" measures, and it is much more desirable to design industrial systems such that potential water pollutants are not even generated.

Industrial operations should be designed to prevent production of liquid water-based or organic solvent-based wastes that may have to be sent to a waste processor. Under current conditions, the largest single constituent of so-called "hazardous wastes" is water. Elimination of water from the waste stream automatically prevents pollution and reduces amounts of wastes requiring disposal. The solvents in organic wastes largely represent potentially recyclable or combustible constituents. A properly designed industrial ecosystem does not allow such wastes to be generated or to leave the factory site.

In addition to liquid wastes, many solid wastes must be considered in an industrial ecosystem. The most troublesome are toxic solids that must be placed in a secure hazardous-waste landfill. The problem has become especially acute in some industrialized nations in which the availability of landfill space is severely limited. In a general sense, solid wastes are simply resources that have not been properly utilized. Closer cooperation among suppliers, manufacturers, consumers, regulators, and recyclers can minimize quantities and hazards of solid wastes.

Whenever energy is expended, there is a degree of environmental damage. Therefore, energy efficiency has a high priority in a properly designed industrial ecosystem. Significant progress has been made in this area in recent decades, as much because of the high costs of energy as for environmental improvement. More-efficient devices, such as electric motors, and approaches, such as congeneration of electricity and heat, that make the best possible use of energy resources are highly favored. An important side benefit of more-efficient energy utilization is the lowered emissions of air pollutants, including greenhouse gases.

19.8 THREE KEY ATTRIBUTES: ENERGY, MATERIALS, DIVERSITY

By analogy with biological ecosystems, a successful industrial ecosystem should have (1) renewable energy, (2) complete recyling of materials, and (3) species diversity for resistance to external shocks. These three key characteristics of industrial ecosystems are addressed here.

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Unlimited Energy

Energy is obviously a key ingredient of an industrial ecosystem. Unlike materials, the flow of energy in even a well-balanced closed industrial ecosystem is essentially one-way in that energy enters in a concentrated, highly usable form, such as chemical energy in natural gas, and leaves in a dilute, disperse form as waste heat. An exception is the energy that is stored in materials. This can be in the form of energy that can be obtained from materials, such as by burning rubber tires, or it can be in the form of what might be called "energy credit," which means that by using a material in its refined form, energy is not consumed in making the material from its raw material precursors. A prime example of this is the "energy credit" in metals, such as that in aluminum metal, which can be refined into new aluminum objects requiring only a fraction of the energy consumed to refine the metal from aluminum ore. On the other hand, recycling and reclaiming some materials can require a lot of energy, and the energy consumption of a good closed industrial ecosystem can be rather high.

Given the needed elements, any material can be made if a sufficient amount of energy is available. The key energy requirement is a source that is abundant and of high quality, that can be used efficiently, and that does not produce unacceptable by-products.

Although energy is ultimately dissipated from an industrial ecosystem, it may go through two or more levels of use before it is wasted. An example of this would be energy from natural gas burned in a turbine linked to a generator, the exhaust gases used to raise steam in a power plant to run a steam turbine, and the relatively cool steam from the turbine used to heat buildings.

Natural ecosystems run on unlimited, renewable energy from the sun or, in some specialized cases, from geochemical sources. Successful industrial ecosystems must also have sources of energy that are not severely limited by either supply or potential for environmental damage in order to be sustained for an indefinite period of time. The obvious choice for such an energy source would seem to be solar energy. However, solar sources present formidable problems, not the least of which is that they work poorly during those times of the day and seasons of the year when the sun does not shine. Even under optimum conditions, solar energy has a low power density necessitating collection and distribution systems of an unprecedented scale if they are going to displace present fossil energy sources. Other renewable sources, such as wind, tidal, geothermal, biomass, and hydropower present similar challenges. It is likely, therefore, that fossil energy sources will provide a large share of the energy for industrial ecosystems in the foreseeable future. This assumes that a way can be found to manage greenhouse gases. At the present time, it appears that injection of carbon dioxide from combustion into deep ocean regions is the only viable alternative for sequestering carbon dioxide, and this approach remains an unproven technology on a large scale. (One potential problem is that the slight increase in ocean water pH of about $^1/_{10}$ pH unit could be detrimental to many of the organisms that live in the ocean.)

Nuclear fusion power remains a tantalizing possibility for unlimited energy, but so far practical nuclear fusion reactors for power generation have proven an elusive target. Unattractive as it is to many, the only certain, environmentally acceptable

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energy source that can without question fill the energy needs of modern industrial ecology systems is nuclear fission energy. With breeder reactors that can generate additionalfissionable material from essentially unlimited supplies of uranium-238, nuclear fission can meet humankind's energy needs for the foreseeable future. Of course, there are problems with nuclear fission—more political and regulatory than technical. The solution to these problems remains a central challenge for humans in the modern era.

Industrial Ecology and Material Resources

A system of industrial ecology is successful if it reduces demand for materials from virgin sources. Strategies for reduced material use may be driven by technology, by economics, or by regulation. The four major ways in which material consumption can be reduced are (1) using less of a material for a specific application, an approach called **dematerialization**; (2) **substitution** of a relatively more abundant and safe material for one that is scarce or toxic; (3) **recycling**, broadly defined; and (4) extraction of useful materials from wastes, sometimes called **waste mining**. These four facets of efficient materials utilization are outlined in this section.

Dematerialization

There are numerous recent examples of reduced uses of materials for specific applications. One example of dematerialization is the transmission of greater electrical power loads with less copper wire by using higher voltages on long distance transmission lines. Copper is also used much more efficiently for communications transmission than it was in the early days of telegraphy and telephone communication. Amounts of silver used per roll of photographic film have decreased significantly in recent years. The layer of tin plated onto the surface of a "tin can" used for food preservation and storage is much lower now than it was several decades ago. In response to the need for greater fuel economy, the quantities of materials used in automobiles have decreased significantly over the last 2 decades, a trend reversed, unfortunately, by the more recent increased popularity of large "sport utility vehicles." Automobile storage batteries now use much less lead for the same amount of capacity than they did in former years. The switch from 6-volt to 12-volt auto batteries in the 1950s enabled use of lighter wires, such as those from the battery to the electrical starter. Somewhat later, the change to steel-belted radial tires enabled use of lighter tires and resulted in greatly increased tire lifetimes so that much less rubber was used for tires.

One of the most commonly cited examples of dematerialization is that resulting from the change from vacuum tubes to solid state circuit devices. Actually, this conversion should be regarded as material substitution, as transistors replaced vacuum tubes, followed by spectacular mass reductions as solid state circuit technology advanced.

Dematerialization can be expected to continue as technical advances, some rapid and spectacular, others slow and incremental, continue to be made. Some industries lead the way out of necessity. Aircraft weight has always played a crucial role in determining performance, so the aircraft manufacturing sector is one of the leaders in dematerialization.

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Substitution of Materials

Substitution and dematerialization are complementary approaches to reducing materials use. The substitution of solid state components for electronic vacuum tubes and the accompanying reduction in material quantities has already been cited. The substitution of polyvinylchloride (PVC) siding in place of wood on houses has resulted in dematerialization over the long term because the plastic siding does not require paint.

Technology and economics combined have been leading factors in materials substitution. For example, the technology to make PVC pipe for water and drain lines has enabled its use in place of more expensive cast iron, copper, and even lead pipe (in the last case, toxicity from lead contamination of water is also a factor to be considered).

A very significant substitution that has taken place over recent decades is that of aluminum for copper and other substances. Copper, although not a strategically short metal resource, nevertheless is not one of the more abundant metals in relation to the demand for it. Considering its abundance in the geosphere and in sources such as coal ash, aluminum is a very abundant metal. Now aluminum is used in place of copper in many high voltage electrical transmission applications. Aluminum is also used in place of brass, a copper-containing alloy, in a number of applications. Aluminum roofing substitutes for copper in building construction. Aluminum cans are used for beverages in place of tin-plated steel cans.

There have been a number of subsitutions of chemicals in recent years, many of them driven by environmental concerns and regulations resulting from those concerns. One of the greater of these has been the substitution of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) for chlorofluorocarbons (Freons or CFCs) driven by concerns over stratospheric ozone depletion. Substitutions of nonhalogenated solvents, supercritical fluid carbon dioxide, and even water with appropriate additives for chlorinated hydrocarbon solvents will continue as environmental concerns over these solvents increase.

Substitutions for metal-containing chemicals promise to reduce costs and toxicities. One such substitution that has greatly reduced the possibilities for lead poisoning is the use of titanium-based pigments in place of lead for white paints. In addition to lead, cadmium, chromium, and zinc are also used in pigments, and substitution of organic pigments for these metals in paints has reduced toxicity risks. Copper, chromium, and arsenic are used in treated wood (CCA lumber). Because of the toxicity of arsenic, particularly, it would be advisable to develop substitutes for these metals in wood. It should be pointed out, however, that the production of practically indestructible CCA lumber has resulted in much less use of wood, and has saved the materials and energy required to replace wood that has rotted or been damaged by termites.

Recycling

For a true and complete industrial ecosystem, close to 100% recycling of materials must be realized. In principle, given a finite supply of all the required elements and

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abundant energy, essentially complete recycling can be achieved. A central goal of industrial ecology is to develop efficient technologies for recycling that reduce the need for virgin materials to the lowest possible levels. Another goal must be to implement process changes that eliminate dissipative uses of toxic substances, such as heavy metals, that are not biodegradable and that pose a threat to the environment when they are discarded.

For consideration of recycling, matter can be put into four separate categories. The first of these consists of elements that occur abundantly and naturally in essentially unlimited quantities in consumable products. Food is the ultimate consumable product. Soap is consumed for cleaning purposes, discarded down the drain, precipitated as its insoluble calcium salt, then finally biodegraded. Materials in this category of recyclables are discharged into the environment and recycled through natural processes or for very low-value applications, such as sewage sludge used as fertilizer on soil.

A second category of recyclable materials consists of elements that are not in short supply, but are in a form that is especially amenable to recycling. Wood is one such commodity. At least a portion of wood taken from buildings that are being razed could and should be recycled. The best example of a kind of commodity in this class is paper. Paper fibers can be recycled up to five times, and the nature of paper is such that it is readily recycled. More than 1/3 of world paper production is currently from recycled sources, and that fraction should exceed 50% within the next several decades. The major impetus for paper recycling is not a shortage of wood to make virgin paper, but rather a shortage of landfill space for waste paper.

A third category of recyclables consists of those elements, mostly metals, for which world resources are low. Chromium and the platinum group of precious metals are examples of such elements. Given maximum incentives to recycle, especially through the mechanism of higher prices, it is likely that virgin sources of these metals can make up any shortfall not met by recycling in the foreseeable future.

A fourth category of materials to consider for recycling consists of parts and apparatus, such as auto parts discussed previously. In many cases, such parts can be refurbished and reused. Even when this is not the case, substantial monetary deposits collected from customers at the time of purchase can provide incentives for recycling. For components to be recycled efficiently and easily, they must be designed with reuse in mind in aspects such as facile disassembly. Such an approach has been called “design for environment,” DFE, and is discussed in more detail in Section 19.10.

Combustion to produce energy can be a form of recycling. For some kinds of materials, combustion in a power plant is the most cost-effective and environmentally safe way of dealing with materials. This is true, for example, of municipal refuse that contains a significant energy value because of combustible materials in it as well as a variety of items that potentially could be recycled for the materials in them. However, once such items become mixed in municipal refuse and contaminated with impurities, the best means of dealing with them is simply combustion.

It should be noted that recycling comes with its own set of environmental concerns. One of the greatest of these is contamination of recycled materials with toxic substances. In some cases, motor oil, especially that collected from the individual consumer sector, can be contaminated with organohalide solvents and other troublesome impurities. Food containers pick up an array of contaminants and, as a

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consequence, recycled plastic is not generally regarded as a good material for food applications. Substances may become so mixed with use that recycling is not practical. This occurs particularly with synthetic fibers, but it may be a problem with plastics, glass, and other kinds of recyclable materials.

Extraction of Useful Materials from Wastes

Sometimes called waste mining, the extraction of useful materials from wastes has some significant, largely unrealized potential for the reduction in use of virgin materials. Waste mining can often take advantage of the costs that must necessarily be incurred in treating wastes, such as flue gases. Sulfur is one of the best examples of a material that is now commonly recovered from wastes. Sulfur is a constituent of all coal and can be recovered from flue gas produced by coal combustion. It would not be cost-effective to use flue gas simply as a source of sulfur. However, since removal of sulfur dioxide from flue gas is now required by regulation, the incremental cost of recovering sulfur as a commodity, rather than simply discarding it, can make sulfur recovery economically feasible.

There are several advantages to recovering a useful resource from wastes. One of these is the reduced need to extract the resource from a primary source. Therefore, every kilogram of sulfur recovered from flue gas means one less kg of sulfur that must be extracted from sulfur ore sources. By using waste sources, the primary source is preserved for future use. Another advantage is that extraction of a resource from a waste stream can reduce the toxicity or potential environmental harm from the waste stream. The removal of arsenic byproduct from the residues of refining some metals that occur with arsenic significantly reduces the toxicities and potential environmental harm by the wastes. Coal ash, the residue remaining after the combustion of coal for power generation, could be used as a source of iron (ferrosilicon), silicon, and aluminum, and perhaps several other elements as well. An advantage of using coal ash in such applications is its physical form. For most power applications, the feed coal is finely ground, so that the ash is in the form of a powder. This means that coal ash is already in the physical form most amenable to processing for byproducts recovery. For a particular coal feedstock, coal ash is homogeneous, which offers some definite advantages in processing and resource recovery. A third advantage of coal ash is that it is anhydrous, so no additional energy needs to be expended in removing water from an ore.

Diversity and Robust Character of Industrial Ecosystems

Successful natural ecosystems are highly diverse, as a consequence of which they are also very **robust**. Robustness means that if one part of the system is perturbed, there are others that can take its place. Consider what happens if the numbers of a top predator at the top of a food chain in a natural ecosystem are severely reduced because of disease. If the system is well balanced, another top predator is available to take its place.

The energy sector of industrial ecosystems often suffers from a lack of robustness. Examples of energy vulnerability have become obvious with several “energy crises” during recent history. Another requirement of a healthy industrial ecology system that is vulnerable in some societies is water. In some regions of the world, both the

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quantity and quality of water are severely limited. A lack of self-sufficiency in food is a third example of vulnerability. Vulnerabililty in food and water are both strongly dependent upon climate, which in turn is tied to environmental concerns as a whole.

19.9 LIFE CYCLES: EXPANDING AND CLOSING THE MATERIALS LOOP

In a general sense, the traditional view of product utilization is the one-way process of extraction → production → consumption → disposal shown in the upper portion of Figure 19.6. Materials that are extracted and refined are incorporated into the production of useful items, usually by processes that produce large quant-ities of waste by-products. After the products are worn out, they are discarded. This essentially one-way path results in a relatively large exploitation of resources, such as metal ores, and a constant accumulation of wastes. As shown at the bottom of Figure 19.6, however, the one-way path outlined above can become a cycle in which manufactured goods are used, then recycled at the end of their life spans. As

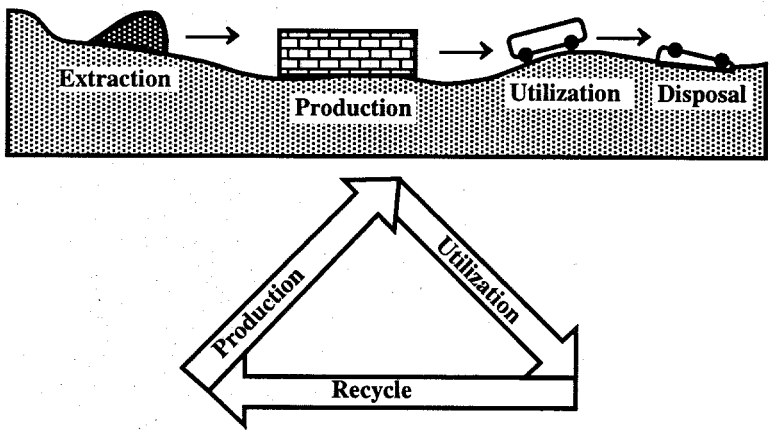


Figure 19.6 The one-way path of conventional utilization of resources to make manufactured goods followed by disposal of the materials and goods at the end consumes large quantities of materials and makes large quantities of wastes (top). In an ideal industrial ecosystem (bottom), the loop is closed and spent products are recycled to the production phase.

one aspect of such a cyclic system, it is often useful for manufacturers to assume responsibility for their products, to maintain "stewardship." Ideally, in such a system a product or the material in it would have a never-ending life cycle; when its useful lifetime is exhausted, it is either refurbished or converted into another product.

In considering life cycles, it is important to note that commerce can be divided into the two broad categories of **products** and **services**. Whereas most commercial activity used to be concentrated on providing large quantities of goods and products, demand has been largely satisfied for some segments of the population, and the wealthier economies are moving more to a service-based system. Much of the commerce required for a modern society consists of a mixture of services and goods. The trend toward a service economy offers two major advantages with respect to wasteminimization. Obviously, a pure service involves little material, and a service provider is in a much better position to control materials to ensure that they are

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recycled and to control wastes, ensuring their proper disposal. A commonly cited example is that of photocopy machines. They provide a service, and a heavily used copy machine requires frequent maintenance and cleaning. The parts of such a machine and the consumables, such as toner cartridges, consist of materials that eventually will have to be discarded or recycled. In this case, it is often reasonable for the provider to lease the machine to users, taking responsibility for its maintenance and ultimate fate. The idea could even be expanded to include recycling of the paper processed by the copier, with the provider taking responsibility for recyclable paper processed by the machine.

It is usually difficult to recycle products or materials within a single, relatively narrow industry. In most cases, to be practical, recycling must be practiced on a larger scale than simply that of a single industry or product. For example, recycling plastics used in soft drink bottles to make new soft drink bottles is not allowed because of the possibilities for contamination. However, the plastics can be used as raw material for auto parts. Usually, different companies are involved in making auto parts and soft drink bottles.

Product Stewardship

The degree to which products are recycled is strongly affected by the custody of the products. For example, batteries containing cadmium or mercury pose significant pollution problems when they are purchased by the public; used in a variety of devices, such as calculators and cameras; then discarded through a number of channels, including municipal refuse. However, when such batteries are used within a single organization, it is possible to ensure that almost all of them are returned for recycling. In cases such as this, systems of stewardship can be devised in which marketers and manufacturers exercise a high degree of control of the product. This can be done through several means. One is for the manufacturer to retain ownership of the product, as is commonly practiced with photocopy machines. Another mechanism is one in which a significant part of the purchase price is refunded for trade-in of a spent item. This approach could work very well with batteries containing cadmium or mercury. The normal purchase price could be doubled, then discounted to half with the trade-in of a spent battery.

Embedded Utility

Figure 19.7 can be regarded as an “energy/materials pyramid” showing that the amounts of energy and materials involved decrease going from the raw material to the finished product. The implication of this diagram is that significantly less energy, and certainly no more materials, are involved when recycling is performed near the top of the materials flow chain rather than near the bottom.

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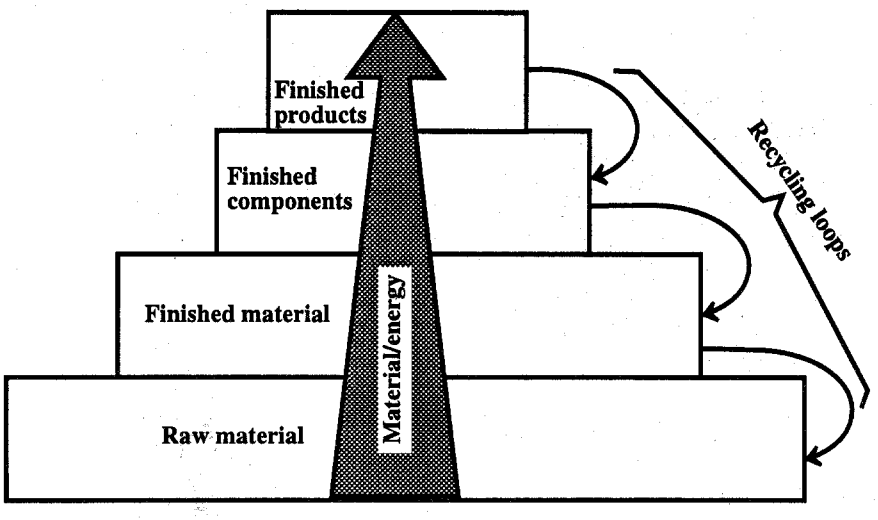


Figure 19.7 A material flow chain or energy/materials pyramid. Less energy and materials are involved when recycling is done near the end of the flow chain, thus retaining embedded utility.

To give a simple example, relatively little energy is required to return a glass beverage bottle from the consumer to the bottler, whereas returning the bottle to the glass manufacturer where it must be melted down and refabricated as a glass container obviously takes a greater amount of energy.

From a thermodynamic standpoint, a final product is relatively more ordered and it is certainly more usable for its intended purpose. The greater usability and lower energy requirements for recycling products higher in the order of material flow are called **embedded utility**. One of the major objectives of a system of industrial ecology and, therefore, one of the main reasons for performing life-cycle assessments is to retain the embedded utility in products by measures such as recycling as near to the end of the material flow as possible, and replacing only those components of systems that are worn out or obsolete. An example of the latter occurred during the 1960s when efficient and safe turboprop engines were retrofitted to still-serviceable commercial aircraft airframes to replace complex piston engines, thus extending the lifetime of the aircraft by a decade or more.

19.10 LIFE-CYCLE ASSESSMENT

From the beginning, industrial ecology must consider process/product design in the management of materials, including the ultimate fates of materials when they are discarded. The product and materials in it should be subjected to an entire **life-cycle assessment** or analysis. A life-cycle assessment applies to products, processes, and services through their entire life cycles from extraction of raw materials—through manufacturing, distribution, and use—to their final fates from the viewpoint of determining, quantifying, and ultimately minimizing their environmental impacts. It takes account of manufacturing, distribution, use, recycling, and disposal. Life-cycle assessment is particularly useful in determining the relative environmental merits of alternative products and services. At the consumer level, this could consist of an

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evaluation of paper versus styrofoam drinking cups. On an industrial scale, life-cycle assessment could involve evaluation of nuclear versus fossil energy-based electrical power plants.

A basic step in life-cycle analysis is **inventory analysis** which provides qualitative and quantitative information regarding consumption of material and energy resources (at the beginning of the cycle) and releases to the anthrosphere, hydrosphere, geosphere, and atmosphere (during or at the end of the cycle). It is based upon various materials cycles and budgets, and it quantifies materials and energy required as input and the benefits and liabilities posed by products. The related area of **impact analysis** provides information about the kind and degree of environmental impacts resulting from a complete life cycle of a product or activity. Once the environmental and resource impacts have been evaluated, it is possible to do an **improvement analysis** to determine measures that can be taken to reduce impacts on the environment or resources.

In making a life-cycle analysis the following must be considered:

- If there is a choice, selection of the kinds of materials that will minimize waste
- Kinds of materials that can be reused or recycled
- Components that can be recycled
- Alternate pathways for the manufacturing process or for various parts of it

Although a complete life-cycle analysis is expensive and time-consuming, it can yield significant returns in lowering environmental impacts, conserving resources, and reducing costs. This is especially true if the analysis is performed at an early stage in the development of a product or service. Improved computerized techniques are making significant advances in the ease and efficacy of life-cycle analyses. Until now, life-cycle assessments have been largely confined to simple materials and products such as reusable cloth vs. disposable paper diapers. A major challenge now is to expand these efforts to more-complex products and systems such as aircraft or electronics products.

Scoping in Life-Cycle Assessment

A crucial early step in life-cycle assessment is **scoping** the process by determining the boundaries of time, space, materials, processes, and products to be considered. Consider as an example the manufacture of parts that are rinsed with an organochloride solvent in which some solvent is lost by evaporation to the atmosphere, by staying on the parts, during the distillation and purification process by which the solvent is made suitable for recycling, and by disposal of waste solvent that cannot be repurified. The scope of the life-cycle assessment could be made very narrow by confining it to the process as it exists. An assessment could be made of the solvent losses, the impacts of these losses, and means for reducing the losses, such as reducing solvent emissions to the atmosphere by installation of activated carbon air filters or reducing losses during purification by employing more-efficient distillation

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processes. A more broadly scoped life-cycle assessment would consider alternatives to the organochloride solvent. An even broader scope would consider whether the parts even need to be manufactured—are there alternatives to their use?

19.11 CONSUMABLE, RECYCLABLE, AND SERVICE (DURABLE) PRODUCTS

In industrial ecology, most treatments of life-cycle analysis make the distinction between **consumable products**, which are essentially used up and dispersed to the environment during their life cycle and **service or durable products**, which essentially remain in their original form after use. Gasoline is clearly a consumable product, whereas the automobile in which it is burned is a service product. It is useful, however, to define a third category of products that clearly become "worn out" when employed for their intended purpose, but which remain largely undispersed to the environment. The motor oil used in an automobile is such a substance in that most of the original material remains after use. Such a category of material may be called a **recyclable commodity**.

Desirable Characteristics of Consumables

Consumable products include laundry detergents, hand soaps, cosmetics, windshield washer fluids, fertilizers, pesticides, laser printer toners, and all other materials that are impossible to reclaim after they are used. The environmental implications of the use of consumables are many and profound. In the late 1960s and early 1970s, for example, nondegradable surfactants in detergents caused severe foaming and esthetic problems at water treatment plants and sewage outflows, and the phosphate builders in the detergents promoted excessive algal growth in receiving waters, resulting in a condition known as eutrophication. Lead in consumable leaded gasoline was widely dispersed to the environment when the gasoline was burned. These problems have now been remedied with the adoption of phosphate-free detergents employing biodegradable surfactants and the mandatory use of unleaded gasoline.

Since they are destined to be dispersed into the environment, consumables should meet several "environmentally friendly" criteria, including the following:

- **Degradability**. This usually means biodegradability, such as that of household detergent constituents that occurs in waste-treatment plants and in the environment. Chemical degradation may also occur.
- **Nonbioaccumulative**. Lipid-soluble, poorly biodegradable substances, such as DDT and PCBs, tend to accumulate in organisms and to be magnified through the food chain. This characteristic should be avoided in consumable substances.
- **Nontoxic**. To the extent possible, consumables should not be toxic in the concentrations that organisms are likely to be exposed to them. In addition to their not being acutely toxic, consumables should not be mutagenic, carcinogenic, or teratogenic (cause birth defects).

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Desirable Characteristics of Recyclables

Recyclables is used here to describe materials that are not used up in the sense that laundry detergents or photocopier toners are consumed, but are not durable items. Recyclables can consist of a variety of chemical substances and formulations. The hydrochlorofluorocarbons (HCFCs) used as refrigerant fluids fall into this category, as does ethylene glycol mixed with water in automobile engine antifreeze/antiboil formulations (although rarely recycled in practice).

Insofar as possible, recyclables should be minimally hazardous with respect to toxicity, flammability, and other hazards. For example, both volatile hydrocarbon solvents and organochloride (chlorinated hydrocarbon) solvents are recyclable after use for parts degreasing and other applications requiring a good solvent for organic materials. The hydrocarbon solvents have relatively low toxicities, but may present flammability hazards during use and reclamation for recycling. The organochloride solvents are less flammable, but may present a greater toxicity hazard. An example of such a solvent is carbon tetrachloride, which is so nonflammable that it was once used in fire extinguishers, but the current applications of which are highly constrained because of its high toxicity.

An obviously important characteristic of recyclables is that they should be designed and formulated to be amenable to recycling. In some cases, there is little leeway in formulating potentially recyclable materials; motor oil, for example, must meet certain criteria, including the ability to lubricate, stand up to high temperatures, and other attributes, regardless of its ultimate fate. In other cases, formulations can be modified to enhance recyclability. For example, the use of bleachable or removable ink in newspapers enhances the recyclability of the newsprint, enabling it to be restored to an acceptable level of brightness.

For some commodities, the potential for recycling is enormous. This can be exemplified by lubricating oils. The volume of motor oil sold in the U.S. each year for gasoline engines is about 2.5 billion liters, a figure that is doubled if all lubricating oils are considered. A particularly important aspect of utilizing recyclables is their collection. In the case of motor oil, collection rates are low from consumers who change their own oil, and they are responsible for the dispersion of large amounts of waste oil to the environment.

Desirable Characteristics of Service Products

Since, in principle at least, service products are destined for recycling, they have comparatively lower constraints on materials and higher constraints on their ultimate disposal. A major impediment to the recycling of service products is the lack of convenient channels through which they can be put into the recycling loop.Television sets and major appliances such as washing machines or ovens have many recyclable components, but often end up in landfills and waste dumps simply because there is no handy means for getting them from the user and into the recycling loop. In such cases, government intervention may be necessary to provide appropriate channels. One partial remedy to the disposal/recycling problem consists of leasing arrangements or payment of deposits on items such as batteries to ensure their return to a recycler. The terms “de-shopping” or “reverse shopping” describe a process by which service

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commodities would be returned to a location such as a parking lot where they could be collected for recycling. According to this scenario, the analogy to a supermarket would be a facility in which service products are disassembled for recycling.

Much can be done in the design of service products to facilitate their recycle. One of the main characteristics of recyclable service products must be ease of disassembly so that remanufacturable components and recyclable materials, such as copper wire, can be readily removed and separated for recycling.

19.12 DESIGN FOR ENVIRONMENT

Design for environment is the term given to the approach of designing and engineering products, processes, and facilities in a manner that minimizes their adverse environmental impacts and, where possible, maximizes their beneficial environmental effects. In modern industrial operations, design for environment is part of a larger scheme termed "design for X," where "X" can be any one of a number of characteristics such as assembly, manufacturability, reliability, and serviceability. In making such a design, numerous desired characteristics of the product must be considered, including ultimate use, properties, costs, and appearance. Design for environment requires that the designs of the product, the process by which it is made, and the facilities involved in making it conform to appropriate environmental goals and limitations imposed by the need to maintain environmental quality. It must also consider the ultimate fate of the product, particularly whether it can be recycled at the end of its normal life span.

Products, Processes, and Facilities

In discussing design for environment, the distinctions among products, processes, and facilities must be kept in clear perspective. **Products**—automobile tires, laundry detergents, and refrigerators—are items sold to consumers. **Processes** are the means of producing products and services. For example, tires are made by a process in which hydrocarbon monomers are polymerized to produce rubber molded in the shape of a tire with a carcass reinforced by synthetic fibers and steel wires. A **facility** is where processes are carried out to produce or deliver products or services. In cases where services are regarded as products, the distinction between products and processes becomes blurred. For example, a lawn-care service delivers products in the forms of fertilizers, pesticides, and grass seeds, but also delivers pure services including mowing, edging, and sod aeration.

Although *products* tend to get the most public attention in consideration of environmental matters, *processes* often have more environmental impact. Successful process designs tend to stay in service for many years and to be used to make a wide range of products. While the product of a process may have minimal environmental impact, the process by which the product is made may have marked environmental effects. An example is the manufacture of paper. The environmental impact of paper as a product, even when improperly discarded, is not terribly great, whereas the process by which it is made involves harvesting wood from forests, high use of water, potential emission of a wide range of air pollutants, and other factors with profound environmental implications.

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Processes develop symbiotic relationships when one provides a product or service utilized in another. An example of such a relationship is that between steel making and the process for the production of oxygen required in the basic oxygen process by which carbon and silicon impurities are oxidized from molten iron to produce steel. The long lifetimes and widespread applicability of popular processes make their design for environment of utmost importance.

The nature of a properly functioning system of industrial ecology is such that processes are even more interwoven than would otherwise be the case, because byproducts from some processes are used by other processes. Therefore, the processes employed in such a system and the interrelationships and interpendencies among them are particularly important. A major change in one process may have a "domino effect" on the others.

Key Factors in Design for Environment

Two key choices that must be made in design for environment are those involvingmaterials and energy. The choices of materials in an automobile illustrate some of the possible tradeoffs. Steel as a component of automobile bodies requires relatively large amounts of energy and involves significant environmental disruption in the mining and processing of iron ore. Steel is a relatively heavy material, so more energy is involved in moving automobiles made of steel. However, steel is durable, is easy to recycle, and is produced initially from abundant sources of iron ore. Aluminum is much lighter than steel and quite durable. It has an excellent percentage of recycling. Good primary sources of aluminum, bauxite ores, are not as abundant as iron ores, and large amounts of energy are required in the primary production of aluminum. Plastics are another source of automotive components. The light weight of plastic reduces automotive fuel consumption, plastics with desired properties are readily made, and molding and shaping plastic parts is a straightforward process. However, plastic automobile components have a low rate of recycling.

Three related characteristics of a product that should be considered in design for environment are durability, repairability, and recyclability. **Durability** simply refers to how well the product lasts and resists breakdown in normal use. Some products are notable for their durability; ancient two-cylinder John Deere farm tractors from the 1930s and 1940s are legendary in farming circles for their durability, enhanced by the affection engendered in their owners, who tend to preserve them. **Repairability** is a measure of how easy and inexpensive it is to repair a product. A product that can be repaired is less likely to be discarded when it ceases to function for some reason. **Recyclability** refers to the degree and ease with which a product or components of it can be recycled. An important aspect of recyclability is the ease with which a product can be disassembled into constituents consisting of a single material that can be recycled. It also considers whether the components are made of materials that can be recycled.

Hazardous Materials in Design for Environment

A key consideration in the practice of design for environment is the reduction of the dispersal of hazardous materials and pollutants. This can entail the reduction or

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elimination of hazardous materials in manufacture, an example of which was the replacement of stratospheric ozone-depleting chlorofluorocarbons (CFCs) in foam blowing of plastics. If appropriate substitutes can be found, somewhat toxic and persistent chlorinated solvents should not be used in manufacturing applications such as parts washing. The use of hazardous materials in the product—such as batteries containing toxic cadmium, mercury, and lead—should be eliminated or minimized. Pigments containing heavy metal cadmium or lead should not be used if there are any possible substitutes. The substitution of hydrochlorofluorocarbons and hydrofluorocarbons for ozone-depleting CFCs in products (refrigerators and air conditioners) is an example of a major reduction in environmentally damaging materials in products. The elimination of extremely persistent polychlorinated biphenyls (PCBs) from electrical transformers removed a major hazardous waste problem due to the use of a common product (although PCB spills and contamination from the misuse and disassembly of old transformers has remained a persistent problem even up to the present).

19.13 OVERVIEW OF AN INTEGRATED INDUSTRIAL ECOSYSTEM

Figure 19.8 provides an overview of an integrated industrial ecosystem including all the components defined and discussed earlier in this chapter. Such a system can be divided into three separate, somewhat overlapping sectors controlled by the following: (1) the raw materials supply and processing sector, (2) the manufacturing sector, and (3) the consumer sector.

There are several important aspects of a complete industrial ecosystem. One of these is that, as discussed in the preceding section, there are several points at which materials can be recycled in the system. A second aspect is that there are several points at which wastes are produced. The potential for the greatest production of waste lies in the earlier stages of the cycle in which large quantities of materials with essentially no use associated with the raw material, such as ore tailings, may require disposal. In many cases, little if anything of value can be obtained from such wastes and the best thing to do with them is to return them to their source (usually a mine), if possible. Another big source of potential wastes, and often the one that causes the most problems, consists of postconsumer wastes generated when a product's life cycle is finished. With a properly designed industrial ecology cycle, such wastes can be be minimized and, ideally, totally eliminated.

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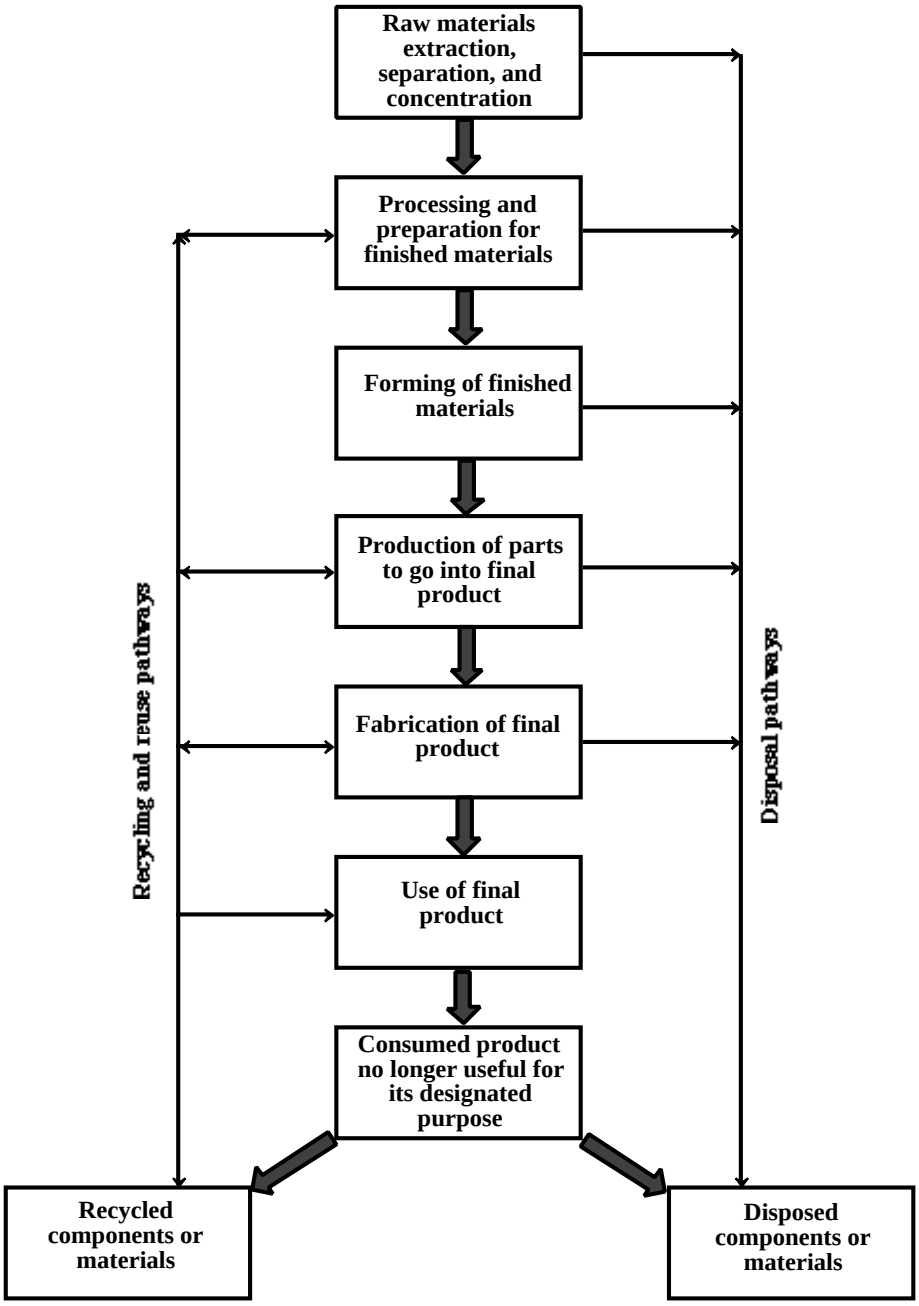


Figure 19.8 Outline of materials flow through a complete industrial ecosystem.

In general, the amount of waste per unit output decreases in going through the industrial ecology cycle from virgin raw material to final consumer product. Also, the amount of energy expended in dealing with waste or in recycling decreases farther into the cycle. For example, waste iron from the milling and forming of automobile

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parts can be recycled from a manufacturer to the primary producer of iron as scrap steel. To be used, such steel must be remelted and run through the steel manufacturing process again, with a considerable consumption of energy. However, a postconsumer item, such as an engine block, can be refurbished and recycled to the market with relatively less expenditure of energy.

At the present time, the three major enterprises in an industrial ecology cycle, the materials producer, the manufacturer, and the consumer, act largely independently of each other. As raw materials become scarcer, there will be more economic incentives for recycling and integration of the total cycle. Furthermore, there is a need for better, morescientifically based regulatory incentives leading to the practice of industrial ecology.

19.14 THE KALUNDBORG EXAMPLE

The most often cited example of a functional industrial ecosystem is that of Kalundborg, Denmark. The various components of the Kalundborg industrial ecosystem are shown in Figure 19.9. To a degree, the Kalundborg system developed spontaneously, without being specifically planned as an industrial ecosystem. It is based upon two major energy suppliers, the 1,500-megawatt ASNAES coal-fired electrical power plant and the 4–5 million tons/year Statoil petroleum refining complex, each the largest of its kind in Denmark. The electric power plant sells process steam to the oil refinery, from which it receives fuel gas and cooling water. Sulfur removed from the petroleum goes to the Kemira sulfuric acid plant. Byproduct heat from the two energy generators is used for district heating of homes and commercial establishments,as well as to heat greenhouses and a fish-farming operation. Steam from the electrical power plant is used by the $2 billion

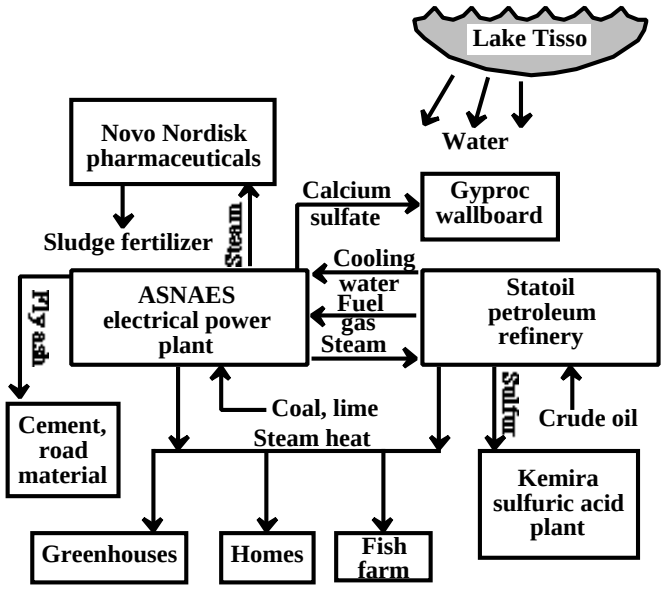


Figure 19.9 Schematic of the industrial ecosystem in Kalundborg, Denmark.

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per year Novo Nordisk pharmaceutical plant, a firm that produces industrial enzymes and 40% of the world's supply of insulin. This plant generates a biological sludge that is used by area farms for fertilizer. Calcium sulfate produced as a byproduct of sulfur removal by lime scrubbing from the electrical plant is used by the Gyproc company to make wallboard. The wallboard manufacturer also uses clean-burning gas from the petroleum refinery as fuel. Fly ash generated from coal combustion goes into cement and roadbed fill. Lake Tisso serves as a freshwater source. Other examples ofefficient materials utilization associated with Kalundborg include use of sludge from the plant that treats water and wastes from the fish farm's processing plant for fertilizer, and blending of excess yeast from Novo Nordisk's insulin production as a supplement to swine feed.

The development of the Kalundborg complex occurred over a long period of time, beginning in the 1960s, and provides some guidelines for the way in which an industrial ecosystem can grow naturally. The first of many synergistic (mutually advantageous) arrangements was cogeneration of usable steam along with electricity by the ASNAES electrical power plant. The steam was first sold to the Statoil petroleum refinery; then, as the advantages of large-scale, centralized production of steam became apparent, steam was also provided to homes, greenhouses, the pharmaceutical plant, and the fish farm. The need to produce electricity more cleanly than was possible simply by burning high-sulfur coal resulted in two more synergies. Installation of a lime-scrubbing unit for sulfur removal on the power plant stack resulted in the production of large quantities of calcium sulfate, which found a market in the manufacture of gypsum wallboard. It was also found that a clean-burning gas by-product of the petroleum refining operation could be substituted in part for the coal burned in the power plant, further reducing pollution.

The implementation of the Kalundborg ecosystem occurred largely because of the close personal contact among the managers of the various facilities in a relatively close social and professional network over a long period of time. All the contracts have been based upon sound business fundamentals and have been bilateral. Each company has acted upon its perceived self-interest, and there has been no master plan for the system as a whole. The regulatory agencies have been cooperative, but not coercive in promoting the system. The industries involved in the agreements have fit well, with the needs of one matching the capabilities of the other in each of the bilateral agreements. The physical distances involved have been small and manageable; it is not economically feasible to ship commodities such as steam or fertilizer sludges for long distances.

19.15 SOCIETAL FACTORS AND THE ENVIRONMENTAL ETHIC

The "consumer society" in which people demand more and more goods, energy-consuming services, and other amenities that are in conflict with resource conservation and environmental improvement runs counter to a good workable system of industrial ecology. Much of the modern lifestyle and corporate ethic is based upon persuading usually willing consumers that they need and deserve more things, and that they should adopt lifestyles that are very damaging to the environment. The conventional wisdom is that consumers are unwilling to significantly change their

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lifestyles and lessen their demands on world resources for the sake of environmental preservation. However, in the few examples in which consumers have been given a chance to exercise good environmental citizenship, there are encouraging examples that they will do so willingly. A prime example of this is the success of paper, glass, and can recycling programs in connection with municipal refuse collection, implemented to extend landfill lifetimes.

Two major requirements for the kind of public ethic that must accompany any universal adoption of systems of industrial ecology are **education** and **opportunity**. Starting at an early age, people need to be educated about the environment and its crucial importance in maintaining the quality of their lives. They need to know about realistic ways, including the principles of industrial ecology, by which their environment can be maintained and improved. The electronic and print media have a very important role to play in educating the public regarding the environment and resources. Given the required knowledge, the majority of people will do the right thing for the environment.

People also need good opportunities for recycling and for general environmental improvement. It is often said that people will not commute by public transit, but of course they will not do so if public transit is not available, or if it is shabby, unreliable, and even dangerous. They will not recycle cans, paper, glass, and other consumer commodities if convenient, well-maintained collection sites are not accessible to them. There are encouraging examples, including some from the United States, that opportunities to contribute to environmental protection and resource conservation will be met with a positive response from the public.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Industrial ecology is defined as [1]_____

_____.
The ways in which an industrial system handles materials and energy, extracting needed materials from sources such as ores, using energy to assemble materials in desired ways, and disassembling materials and components defines [2]_____
_____. A number of industrial enterprises acting synergistically, each utilizing products and potential wastes from other members of the system constitutes [3]_____. Industrial development that can be sustained without environmental damage and to the benefit of all people defines [4]_____
_____. The benefits of a successfully operating industrial ecosystem include [5]_____

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_____.
[6]_____ occurs when firms utilize each other's residual materials, thus forming the basis of relationships between firms in a functional industrial ecosystem. The five major components of an industrial ecosystem are [7]__

_____.
The process that virgin materials entering an industrial system are subjected to starts with [8]_____, followed by [9]_____, additional [10]_____
_____ steps, and finally additional [11]_____
steps leading to the finished materials. Two different recycling streams in the materials processing and manufacturing sector are [12]_____
_____. Industrial metabolism as it is now practiced has a vexing tendency to [13]_____
_____ materials to an extent that they are no longer useful but are still harmful to the environment. A comparison of the metabolisms of natural ecosystems with that of industrial systems as they are commonly encountered shows that the basic unit of a natural ecosystem is [14]_____ whereas that of an industrial ecosystem is [15]_____, recycling in a natural ecosystem is essentially [16]_____ whereas that in an industrial ecosystem is often [17]_____
_____, and the ultimate major function of an organism is [18]_____, whereas that of an industrial system is [19]_____
_____. At the least efficient level of materials utilization in industrial systems, raw materials are viewed as being [20]_____ and no consideration is given to limiting [21]_____ whereas at the most efficient level materials are [22] to the maximum extent possible and there are no [23]_____. In considering the effects of major anthrospheric activities on other environmental spheres, the greatest potential effect of fossil fuel combustion on the atmosphere is [24] the greatest effects of indus-trial manufacturing and processing on the geosphere results from the effects of the [25]_____ industries, the geosphere is affected by crop production because of loss of [26]_____ through the action of wind and water [27]_____, and a major effect on the biosphere of livestock production is [28]_____. Three key attributes of a successful industrial ecosystem are [29]
_____. The four major ways in which material consumption can be reduced are [30]_____
_____. When a natural or industrial ecosystem is such that if one part of the system is perturbed, there are others that can take its place the system is said to be [31]_____. Product stewardship refers to [32]_____
_____.
The greater usability and lower energy requirements for recycling products higher in the order of material flow are called [33]_____. Consideration of process/product design in the management of materials, including the ultimate fates of materials when they are discarded in an industrial operation is referred to as [34]. In doing such an assessment [35]____
_____ provides qualitative and quantitative information regarding

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consumption of material and energy resources (at the beginning of the cycle) and releases to the anthrosphere, hydrosphere, geosphere, and atmosphere (during or at the end of the cycle), [36]_____ provides information about the kind and degree of environmental impacts resulting from a complete life cycle of a product or activity, and an improvement analysis is done to [37]_____ _____.
In doing a life-cycle assessment scoping is done to determine [38]_____ _____.
Products such as laundry detergents, windshield washer fluids, and fertilizers that are impossible to reclaim after they are used are referred to as [39]_____ _____. They should meet the three "environmental friendly" criteria of being [40]_____.
Recyclables is a term used here to describe materials that are not [41]_____ but are also not [42]_____. Recyclables in an automobile include [43]_____ _____. [44]_____ is the term given to the approach of designing and engineering products, processes, and facilities in a manner that minimizes their adverse environmental impacts and, where possible, maximizes their beneficial environmental effects. In discussing design for environment, it is important to distinguish among the three categories of [45] . Three related characteristics of a product that should be considered in design for environment are [46]_____. The most often cited example of a functional industrial ecosystem is that in [47] . It is based upon two major [48]_____. Two major requirements for the kind of public ethic that must accompany any universal adoption of systems of industrial ecology are [49]_____.

Answers to Chapter Summary

1. an approach based upon systems engineering and ecological principles that integrates the production and consumption aspects of the design, production, use, and termination (decommissioning) of products and services in a manner that minimizes environmental impact while optimizing utilization of resources, energy, and capital
2. industrial metabolism
3. an industrial ecosystem
4. sustainable development
5. reduced pollution, high energy efficiency, reduced consumption of virgin materials, maximization of materials recycle, reduction of amounts of wastes, and increased market value of products relative to material and energy consumption.
6. Industrial symbiosis
7. (1) a primary materials producer, (2) a source or sources of energy, (3) a materials processing and manufacturing sector, (4) a waste processing sector, and (5) a consumer sector.
8. extraction
9. concentration
10. refining
11. processing and preparation

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12. process recycle streams external and recycle streams
13. dilute, degrade, and disperse
14. an organism
15. a firm
16. complete
17. very low
18. reproduction
19. production of goods or services
20. unlimited
21. wastes
22. recycled
23. wastes
24. greenhouse warming
25. extractive
26. topsoil
27. erosion
28. loss of species diversity
29. energy, materials, and diversity
30. dematerialization, substitution, recycling, and waste mining
31. robust
32. retention of custody of products to control their fates
33. embedded utility
34. life-cycle assessment
35. inventory analysis
36. impact analysis
37. determine measures that can be taken to reduce impacts on the environment or resources
38. the boundaries of time, space, materials, processes, and products to be considered
39. consumable products
40. degradable, nonbioaccumulative, and nontoxic
41. used up
42. durable items
43. motor oil and antifreeze
44. Design for environment
45. products, processes, and facilities
46. durability, repairability, and recyclability
47. Kalundborg, Denmark
48. energy suppliers
49. education and opportunity

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QUESTIONS AND PROBLEMS

1. In biological ecosystems a process called mineralization occurs as defined in this book. Name and describe a process analogous to mineralization that occurs in an industrial ecosystem.
2. How are the terms industrial metabolism, industrial ecosystem, and sustainable development related to industrial ecology?
3. How is industrial symbiosis related to industrial ecology?
4. Justify or refute the statement that in an operational industrial ecosystem only energy is consumed.
5. In what sense is the consumer sector the most difficult part of an industrial ecosystem?

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6. In what sense might a “moon station” or a colony on Mars advance the practice of industrial ecology?
7. In what sense do modern solid state electronic devices illustrate both dematerialization and material substitution?
8. As applied to material resources, what is the distinction between dematerialization and material substitution? Use the automobile as an example.
9. How does “design for recycling” (DFR) relate to embedded utility?
10. Distinguish among consumable, durable (service), and recyclable products.
11. List some of the “environmentally friendly” criteria met by soap as a consumable commodity.
12. What are the enterprises that serve to underpin the Kalundborg industrial ecosystem? How might they compare with the basic enterprises of an industrial ecosystem consisting of rural counties in the state of Iowa?

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20 GREEN CHEMISTRY FOR A SUSTAINABLE FUTURE

20.1 INTRODUCTION

If one dates the beginnings of chemical industry as a significant economic force from approximately 1850, it is approximately 150 years old. During that time, and particularly during the last half century, this industry has grown to be a huge enterprise fulfilling a large number of human needs and serving to underpin advanced industrialized economies. Because of the potential of this industry to affect all segments of the environment, it can be argued that it is the most significant segment of the anthrosphere. Following the laws of conventional economics, the chemical industry has been directed toward producing more and higher value products at the lowest cost, as measured in conventional economic terms. However, particularly since about the World War II era, it has become increasingly obvious that the practice of industrial chemistry has other costs—environmental costs—not usually measured by the incomplete measures of conventional economics. Some of these costs, such as loss of crop production from the effects of air pollution, have been relatively easy to quantify. Other costs—no less real—have proven difficult to assign a monetary value. These are the costs of damage to the environment and human health resulting from the misuse of chemical processes and products.

In recognition of the environmental effects of the chemical industry and related enterprises, many laws have been passed and implemented throughout the world to regulate chemical processes and products. These laws have emphasized dealing with environmental problems after they have occurred, a "command and control" approach. Compliance with environmental laws over the last several decades has involved the expenditure of more than a trillion dollars worldwide. These laws have unquestionably had some positive effects upon environmental quality, have been effective in helping to save some species from extinction, and have improved human health and quality of life. However, necessary as it is, the regulatory approach to enhancing environmental quality has some definite deficiencies. Its effective implementation and maintenance have required legions of regulators and have resulted in

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the expenditure of vast sums for litigation that could be better used directly to enhance environmental quality. In some cases the regulations have appeared to be petty and poorly cost effective.

A modern industrial society will always require regulations of various kinds to maintain environmental quality and even to ensure its continued existence. But, are there alternatives to some of the regulations? Most desirable are alternatives that help to ensure environmental quality by "natural," self-regulating means. Since about 1990, it has become increasingly evident that, at least to a certain extent, there are alternatives for the chemical industry and associated enterprises through the practice of what has come to be known in the United States and several other countries as **green chemistry**.

What is green chemistry? Perhaps the most straightforward answer to that question is that we are still trying to find out. The term has somewhat different meanings to different people with different perspectives. One definition of green chemistry is "carry out chemical activities—including chemical design, manufacture, use, and disposal—such that hazardous substances will not be used and generated."[1] It must be recognized that the use of hazardous substances is unlikely to ever be totally eliminated. The challenge is to use such substances in a manner that is safe and prevents their dispersal to the environment. With this in mind, green chemistry can be defined somewhat more broadly as *the sustainable exercise of chemical science and technology within the framework of good practice of industrial ecology such that the use and handling of hazardous substances are minimized and such substances are never released to the environment*. The inclusion of industrial ecology (see Chapter 19) in this definition carries with it a number of implications regarding minimum consumption of raw materials, maximum recycling of materials, minimum production of unusable byproducts, and other environmentally friendly factors.

A key aspect of green chemistry is **sustainability**. Ideally, green chemistry is self-sustaining for several reasons. One of these is economic because green chemistry in its most developed form is less costly in strictly monetary terms than chemistry the way it has been traditionally practiced. Green chemistry is sustainable in terms of materials because of its minimum efficient use of raw materials. And green chemistry is sustainable in terms of wastes, because it does not cause an intolerable accumulation of hazardous-waste products.

In implementing the practice of green chemistry, two often-complementary approaches are the following:

- Use existing chemicals, but make them by environmentally benign syntheses.
- Substitute chemicals made by environmentally benign syntheses for existing chemicals.

Both approaches need to be used. And both approaches challenge the ingenuity of chemists and chemical engineers to come up with innovative solutions to environmental problems arising from the chemical industry.

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20.2 THE KEY CONCEPT OF ATOM ECONOMY

Although the yield of a product conventionally defined as the percentage conversion of a limiting reagent to the desired product may be quite high, or even reach 100%, the process may still produce large quantities of undesirable byproduct. Therefore, a much better measure of the degree to which a synthesis is consistent with the process of green chemistry is **atom economy** defined as follows:[2]

$$\text{Atom economy} = \frac{\text{Molecular mass desired product}}{\text{Total molecular mass of materials generated}} \tag{20.2.1}$$

The concept of atom economy can be illustrated in general by the reaction,

$$(\text{reagent})_1 + \ldots + (\text{reagent})_n \rightarrow \text{product} + \text{byproduct} \tag{20.2.2}$$

The ultimate in atom economy is achieved when there is no byproduct so that,

$$(\text{reagent})_1 + \ldots + (\text{reagent})_n \rightarrow \text{product (byproduct} = 0) \tag{20.2.3}$$

and all the reagents are contained within the product. Although this is often not achievable in practice, it is desirable to devise reaction schemes such that

$$\text{byproduct} << \text{product} \tag{20.2.4}$$

One of the greater needs in chemical research today is the development of reactions for synthesis that have a high degree of atom economy.[3]

20.3 HAZARD REDUCTION

The practice of green chemistry requires constant efforts to reduce hazards from feedstocks, media, catalysts, and byproducts. Hazards may take a number of different forms. Among the most obvious of these are hazards from flammable or explosive reagents or media, particularly solvents. Materials may also present health hazards, such as the known human carcinogenicity of vinyl chloride used as a raw material in the manufacture of polyvinyl chloride polymers, or symptoms of perypheral neuropathy caused by exposure to light hydrocarbon liquids such as pentane.

Since hazardous substances manifest their hazards largely through their chemical reactions and characteristics, it is convenient to classify them chemically. Although the chemical variability of hazardous substances make such a classification system somewhat inexact, several categories can be defined based upon chemical behavior.[4] These are the following:

- **Combustible** and **flammable** substances, strong reducers that burn readily or violently in the presence of atmospheric oxygen
- **Oxidizers** that provide oxygen for the combustion of reducers
- **Reactive** substances that are likely to undergo rapid, violent reactions, often in an unpredictable manner

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- **Corrosive** substances that are generally sources of H^+ ion or OH^- ion and that tend to react destructively with materials, particularly metals

Some hazardous substances fall into more than one of these groups, which increases the dangers that they pose.

Often the greatest concern with hazardous substances has to do with toxicity. Toxic substances are not so easy to classify in terms of chemical properties as are substances belonging to the classifications listed above. It is more appropriate to classify toxic substances on the basis of their biochemical properties. Of special use in making these classifications are **structure-activity relationships** that relate known structural features and functional groups to likely toxic effects.

Three kinds of hazardous substances stand out as candidates for reduction in the practice of green chemistry. The first of these consists of **heavy metals**, such as lead, mercury, or cadmium. As elements, these substances are indestructible. They have a wide range of adverse biological effects. Another category consists of **persistent**, **nonbiodegradable organic materials**, such as polychlorinated biphenyls, PCBs. Often not extremely toxic, these substances persist in the environment and exhibit a tendency to become magnified through biological food chains, adversely affecting organisms at or near the end of the food chain. The classic example of such compounds is insecticidal DDT, which caused reproductive problems for birds, such as falcons or eagles, at the top of the food chain. A third category of troublesome hazardous substances consists of **volatile organic compounds**, **VOCs**. These have been particularly prevalent in industrial settings because of their uses as solvents for organic reactions, vehicles in paints and coatings, and for cleaning parts. In the latter two applications, the most convenient means of dealing with these volatile materials was to allow them to evaporate, so that large quantities were simply discharged to the atmosphere.

Regardless of the kind of hazard posed by a substance, a major goal of the practice of green chemistry is to avoid having to deal with such substances in any way. Although this is an idealistic and largely unrealizable target in practice, having it as the ultimate goal serves as a good framework for the practice of benign and sustainable chemistry. Insofar as hazardous substances are concerned, the practice of green chemistry requires: (1) don't use them, (2) don't make them, and (3), if (1) and/or (2) cannot be avoided, never release hazardous substances to the environment.

20.4 FEEDSTOCKS

A crucial decision that must be made in implementing a process to manufacture a chemical or product is selection of **feedstock**. To the extent possible, the feedstock should place minimal demands on Earth's resources. It should be as safe as possible, and its acquisition and refining should be safe. In some cases the processes and reagents required to isolate an otherwise safe feedstock make its acquisition hazardous, such as in the use of highly toxic cyanide to remove low levels of gold from ore. Wherever possible, a feedstock should be *renewable*; for example feedstocks from biomass that can be grown repeatedly are often preferable to depletable petroleum feedstocks.

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In a generalized sense, the overall process of obtaining a useful product from a feedstock, such as petroleum or biological materials, can be divided into the three categories shown in Figure 20.1. Both the petroleum and biological sources of potential feedstocks are relatively well known. For petroleum feedstocks, the technology for separation has been developed to a high degree of sophistication. The technologies for obtaining raw materials from plant sources, such as extraction of oils with solvents or separation of cellulose from lignin in wood, are well advanced. Because of the high degree of development of the petrochemical industry, the science of converting petroleum feedstocks to desired products is very well developed, but is less so in the case of biological feedstocks.

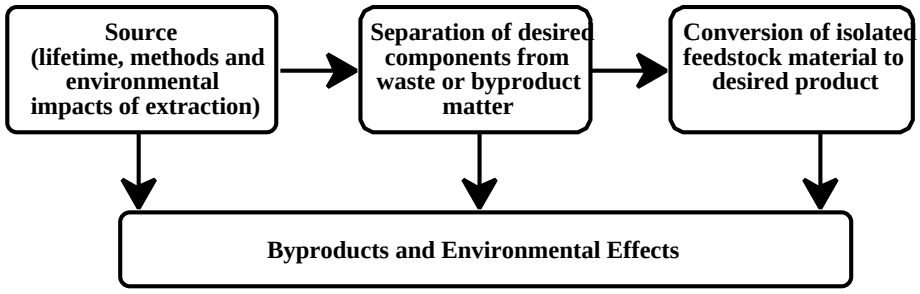


Figure 20.1 The three major steps in obtaining a feedstock and converting it to a useful product. Each of these steps has environmental implications and can benefit from the application of the principles of green chemistry.

Biological Feedstocks

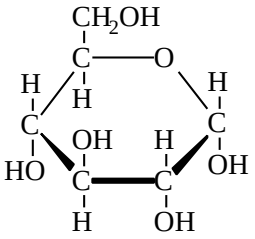
With some billions of tons of carbon fixed as biomass each year, there exists an enormous potential for the use of biological materials as feedstocks. The most obvious such material consists of wood from trees. Large quantities of cellulose are generated each year in the production of crops such as corn and wheat. Although a fraction of crop byproduct biomass should be returned to soil to maintain its condition as a growth medium for plants, there is a substantial excess that could be used as feedstock. Biological processes, particularly plant growth, produce a number of potentially useful biopolymers including, in addition to cellulose, hemicellulose, starch, lignin, and proteins. Plants are also useful sources of smaller molecules, including monosaccharides (glucose), disaccharides (sucrose), amino acids, waxes, fats, oils, and terpene hydrocarbons, including those used to make natural rubber. The potential of genetic engineering to produce plants that have high yields of feedstock chemicals could lead to the development of exciting new sources of biological feedstocks.

Potential feedstocks from biological sources tend to be more complex than those from petroleum. This offers the advantage of starting with a material in which much of the synthesis required to make a product has already been done by a living plant. Furthermore, many desired products have relatively high oxygen contents, and biological materials tend to contain bound oxygen. This can avoid the operation of converting a petroleum-based hydrocarbon feedstock to an oxygenated compound, which often requires severe conditions, hazardous oxidizing agents, and potentially

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troublesome catalysts. In some cases, however, the complexity of biological feedstocks is a disadvantage because it is usually more difficult to convert a complex molecule to a significantly different one than it is to use a relatively simple feedstock.

Arguably the most important biological raw materials for chemical synthesis are carbohydrates produced by plants, including glucose, fructose, sucrose, and starch.



Glucose molecule

Carbohydrates, such as starch from corn grain and sucrose from sugar cane, are generated in high quantities by a number of plants. Furthermore, cellulosic wastes can be hydrolyzed to generate simple sugars that can be used in chemical synthesis. A major advantage of carbohydrates in chemical synthesis is their abundance of hydroxyl functional groups, as shown in the structure of glucose above. Such functionality provides sites for the attachment of other functionalities and for initiating chemical reactions leading to desired products. The inherent biodegradability of carbohydrates provides them with some environmental advantages as well.

In addition to cellulose, a very abundant material in wood is lignin, a complex binding material that serves to hold wood together. Lignin is a biopolymer containing groups such as those shown in Figure 20.2. Unlike carbohydrate cellulose, which has a uniform structure and is composed entirely of glucose monomer units, lignin

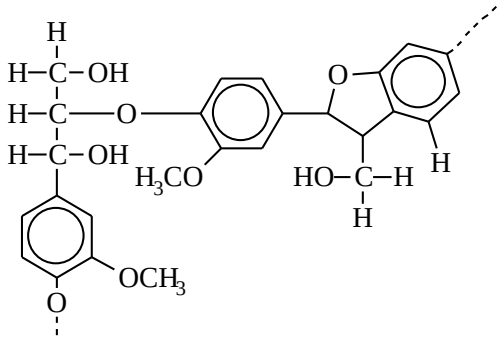


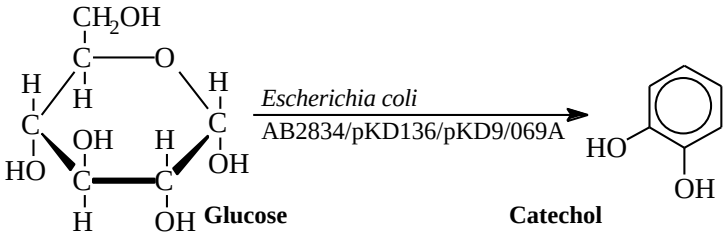
Figure 20.2 Segment of lignin polymer.

has a variable structure. This is a severe detriment to its use as a chemical feedstock. One of the more promising potential uses for abundant lignin resources is the production of phenolic compounds. A major detriment to the use of lignin in green chemistry is its resistance to any sort of biological processes that might be considered for its conversion to useful products.

A potentially important chemical reagent that can be synthesized from glucose by biological means is catechol. Catechol is used to make a wide range of pharmaceutical chemicals, pesticides, antioxidants, and other chemical feedstocks. The

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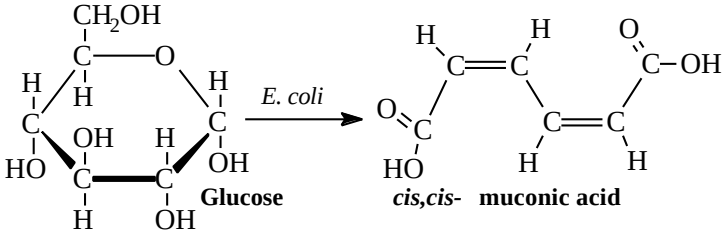
standard synthesis of catechol involves using petroleum-derived benzene and propylene to make cumene, elimination of acetone from cumene by treatment with oxygen to give phenol, then oxidation of phenol to catechol with 70% hydrogen peroxide. These steps require some rather severe conditions, involve toxic benzene feedstock and toxic phenol intermediate, and require stringent precautions in handling highly reactive hydrogen peroxide. Through elegant genetic manipulation, *E. coli* AB2834/pKD136/pKD9/069A, a strain of *Escherichia coli* bacteria, has been developed that catalyzes the following overall biotransformation:



Glucose **Catechol** (20.4.1)

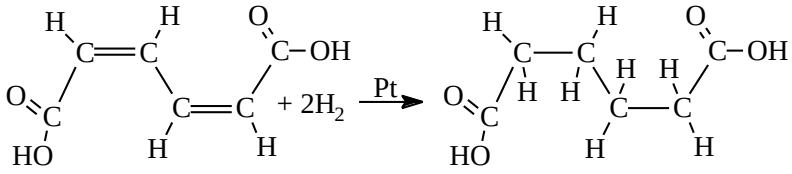
A variation of the biosynthesis described above can be used to make adipic acid, a key feedstock in the manufacture of nylon 6,6. As with catechol, the conventional chemical synthesis of adipic acid commonly starts with benzene, which is hydrogenated to cyclohexane. Air oxidation of cyclohexane over metal catalysts yields cyclohexanol and byproduct cyclohexanone. The oxidation of cyclohexanol with 60% nitric acid yields adipic acid. Elevated temperature (250˚C), high pressure (50 atm), and the use of strong oxidant nitric acid, which carries with it the possibility of nitrogen oxides release, are problems with the synthesis.

As an alternative biological synthesis of adipic acid, a microbial process that uses a genetically engineered strain of bacteria given the designation *Escherichia coli* AB2834/pKD136/pKD8.243A, was developed capable of converting glucose to *cis*-*cis*-muconic acid by way of a catechol intermediate



Glucose ***cis,cis*- muconic acid** (20.4.2)

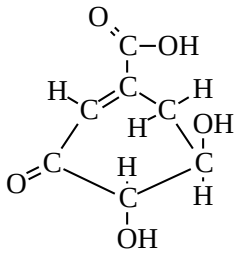
Hydrogenation at a pressure of only 3 atm over a platinum catalyst can then be used to convert the *cis,cis*-muconic acid to adipic acid:



***Cis,cis*- muconic acid** **Adipic acid** (20.4.3)

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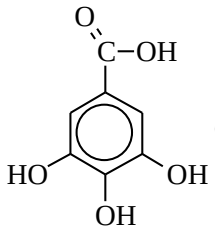
3-Dehydroshikimic acid is a substance that can now be made by environmentally benign biological synthesis. This substance has the potential to substitute for substances made by less environmentally friendly means as a feedstock and as an antioxidant. As shown by its formula,



3-Dehydroshikimic acid

3-dehydroshikimic acid is a hydroaromatic compound. It is an intermediate in the biosynthesis of aromatic amino acids, adipic acid, catechol, gallic acid, and vanillin. This compound has been synthesized biologically in significant yields with genetically modified *Escherichia coli* strain KL3 using as a feedstock glucose as well as a mixture of D-glucose, D-xylose and L-arabinose.[5] This suggests the possibility of biosynthesis of 3-dehydroshikimic acid as a raw material for the manufacture of other organic compounds.

The facile biosynthesis of 3-dehydroshikimic acid and its ability to act as an antioxidant suggest that it may become an important antioxidant. Such antioxidants are added to foods, oils, fats, fuels and lubricants to prevent their being oxidized by reacting with oxygen and reactive intermediates in the oxidation process. At present, the most commonly used antioxidants are butylated hydroxytoluene, synthesized from petroleum feedstocks, and propyl gallate made from gallic acid,



Gallic acid

which is derived from natural source gall nuts or tara powder.

20.5 REAGENTS

Judicious selection of **reagents** and **media** for carrying out chemical processes can be a crucial factor in developing a successful green chemistry process. Use of a benign feedstock may be of relatively little use if large quantities of hazardous reagents are required for its processing. Media, which frequently consist of solvents, are discussed in more detail in Section 20.6.

Two important factors driving reagent selection are **product selectivity** and **product yield**. High-product selectivity means higher conversion of raw material to the desired product. High-product yield means a high percentage of the desired product is obtained relative to the maximum yield calculated from stoichiometric considerations. Both high-product selectivity and high-product yield reduce the amounts of extraneous material that must be handled and separated.

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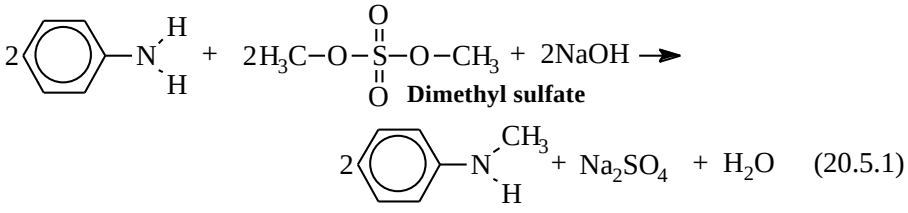
In selecting safe media and feedstocks, consideration of structure-activity relationships can be very useful. It is known that certain structures or functional groups tend to create particular kinds of hazards. For example, the presence of oxygen and nitrogen—particularly multiple nitrogen atoms—in proximity in a molecule tends to make it reactive or even explosive. The presence of the N–N=O functional group results in **N-nitroso** compounds (**nitrosamines**), many of which are carcinogenic. The presence of chemical structures that can result in donation of methyl groups to biomolecules may make a compound mutagenic or carcinogenic; substitution of longer-chain hydrocarbon groups can reduce this hazard.

In evaluating the safety of reagents and choosing safer alternatives, special attention should be given to **functional groups** consisting of particular groupings of atoms. The carcinogenic potential of the N–N=O group was mentioned above. Aldehydes tend to be irritants to animals and are photochemically active, so that they can contribute to smog formation when released to the atmosphere. Whenever possible it is best to use alternative compounds when particular functional groups are likely to be a problem. It is also sometimes possible to mask functional groups to produce less dangerous forms, then unmask them at the point in the synthesis where the functionality is needed.

Oxidation is one of the most common operations in chemical synthesis. The nature of oxidation often requires harsh conditions and harsh reagents, such as permanganate (MnO_4^-), chromium(VI) compounds (such as potassium dichromate, $K_2Cr_2O_7$), toxic and costly osmium tetroxide, or *m*-chloroperbenzoic acid. Therefore, one of the main objectives of green chemistry has been the development of more benign oxidizing agents and oxidation reactions.

Reduction is a common operation in chemical synthesis. As with oxidation, the reagents used for reduction tend to be reactive and difficult to handle. Two of the most common such reagents are lithium aluminum hydride and tributyltin hydride. $LiAlH_4$ is rather hazardous to use. Tributyltin hydride can release volatile tin-containing products that pose toxicity hazards. Both oxidizing and reducing agents used in chemical synthesis produce byproducts that must be carefully disposed of at significant expense.

Alkylation consists of the attachment of alkyl groups, such as the methyl group, $-CH_3$, to an organic molecule. The attachment of an alkyl group to a nitrogen in an amine is used as a step in the synthesis of a variety of dyes, pharmaceuticals, pesticides, plant growth regulators, and other specialty chemicals. In such cases, alkylation is commonly carried out using alkyl halides or alkyl sulfates in the presence of a base as shown below for the attachment of a methyl group to N in aniline:

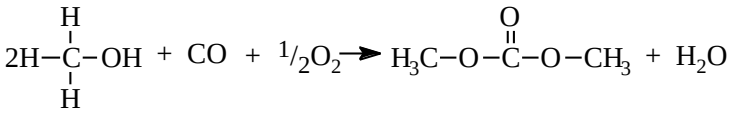


(20.5.1)

This kind of reaction produces significant amounts of inorganic salt byproduct, such as Na_2SO_4. also, alkyl halides and alkyl sulfates pose toxicity concerns; dimethyl sulfate is a primary carcinogen, causing cancer without the need for bioactivation.

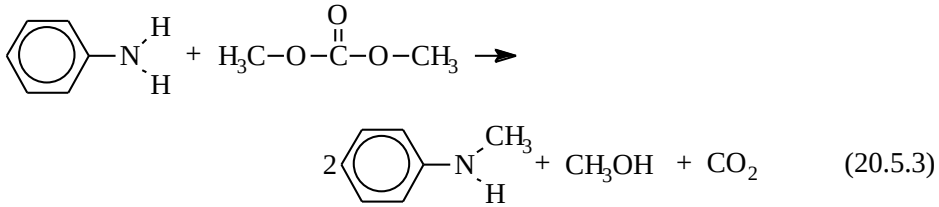
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Relatively nontoxic dialkyl carbonates are very effective alkylating agents that promise to provide a safer alternative to alkyl halides or sulfates for some kinds of alkylation reactions.[6] The promise of dimethyl carbonate for methylation (alkylation in which the methyl group, $-CH_3$, is attached) has been enhanced by the straightforward synthesis of this compound from methanol and carbon monoxide in the presence of a copper salt:



(20.5.2)

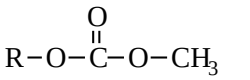
Dimethyl carbonate can be used for methylation of nitrogen in amine compounds at a temperature of 180˚C under continuous-flow gas-liquid phase-transfer catalysis conditions (which involve transfer of organic ionic reactant species between water and an organic phase) as shown below for the methylation of aniline:



(20.5.3)

The use of dimethyl carbonate as a methylating agent offers the twin advantages of up to 99% efficiency of conversion to product with selectivities of 99% or more for the monomethyl product. The byproducts are innocuous carbon dioxide and methanol, which can be recirculated through the process for making dimethyl carbonate (Reaction 20.5.2). Dimethyl carbonate is useful, for example, in making monomethyl organonitrogen derivatives required for the synthesis of analgesics, such as Ibuprofen.

Mixed organic carbonates in which a methyl group is attached to the carbonate as is a much larger organic moiety, R,



A mixed organic carbonate

can be very effective methylating agents, as examples, giving anisoles from phenols, and N-methyl aniline from aniline.[7] A major advantage is that the high-molar-mass mixed organic carbonates are much higher boiling than dimethylcarbonate and reactions using them can be run at ambient pressure rather than in pressurized reaction vessels.

20.6 MEDIA

Media is a term used to refer to the matrix in which or on which chemical processes occur. The type and strength of interaction between the media and reactants in a chemical process play a very important role in determining the type, degree, and rate of the process. Although media may include solids upon which reactions take place, by far the most common type of media consists of liquid

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solvents in which reagents are dissolved. Solvents interact to various extents and in various ways with the solutes dissolved in them. An important phenomenon is **solvation**, in which the solvent molecules interact with solute molecules. A common example of this is the attraction of polar water solvent molecules for dissolved cations and anions as shown in Chapter 7, Figure 7.3. This ability makes water an extraordinarily good solvent for ionic substances—acids, bases, and salts—that are commonly used in chemical reactions. The ability of water to form hydrogen bonds is particularly important in its ability to dissolve a wide range of biological materials capable of forming hydrogen bonds.

By their nature, solvents cause more environmental and health problems than do other participants in the chemical synthesis process. Most solvents are volatile and tend to escape into the workplace and atmosphere. Hydrocarbon solvents are flammable and can cause explosive mixtures with air. Released to the atmosphere, they can be instrumental in causing formation of photochemical smog (see Chapter 16). A number of adverse health effects are attributed to solvents. Carbon tetrachloride, CCl_4, causes lipid peroxidation in the body and can cause severe damage to the liver. Benzene causes blood disorders and is suspected of causing leukemia. Volatile C_5-C_7 alkanes damage nerves and can result in a condition known as peripheral neuropathy. The possibility of causing cancer is always a consideration in dealing with solvents in the workplace.

20.7 THE SPECIAL IMPORTANCE OF SOLVENTS

As noted in the preceding section, solvents are a uniquely important type of media in which chemical processes are carried out. Beyond their uses as reaction media, solvents have other uses, particularly in separation, purification, and cleaning. Water is the most abundant and safest solvent and should be used wherever possible. In fact, one of the main objectives of the practice of green chemistry is to convert processes to the use of water solvent wherever possible. However, water is not a suitable solvent for a wide range of organic substances used industrially. Therefore, the use of organic solvents consisting of hydrocarbons and hydrocarbon derivatives, such as chlorinated hydrocarbons, is unavoidable in many cases. In addition to serving as reaction media, organic solvents are used as cleaners, degreasers, and as extractants to remove organic substances from solids. A major use of organic solvents is as the liquid **vehicle** to enable the application, spreading, and impregnation (such as of cloth) of dissolved or suspended dyes and other agents in formulations of paints, coatings, inks, and related materials.

A key consideration in selecting and using a solvent for the proper practice of green chemistry consists of its toxicological and environmental effects on biological systems. This obviously includes toxic effects to humans. Physical properties, such as volatility, density, and solubility, are important in estimating potential environmental and biological effects. Lipophilicity, the tendency to dissolve lipid tissue, is a measure of the ability of a solvent to penetrate skin and hence is an important factor in determining its biological effects. The environmental persistence and biodegradation of solvents should be considered. Special care must be taken to not use or at least prevent the release to the atmosphere of volatile solvents that may become involved in photochemical reactions leading to photochemical smog

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formation. The formerly widespread use of volatile chlorofluorocarbon solvents as blowing agents to produce porous plastics and plastic foams resulted in widespread dissipation of these ozone destroying chlorofluorocarbon vapors to the atmosphere (see Chapter 16, Section 16.4).

Much of the progress that has been made toward the goal of green chemistry has come with replacement of potentially troublesome solvents with less dangerous ones. Some pertinent examples of such replacement are shown in Table 20.1. The best solvent to use, when possible, is water. It is discussed below.

Water, the Greenest Solvent

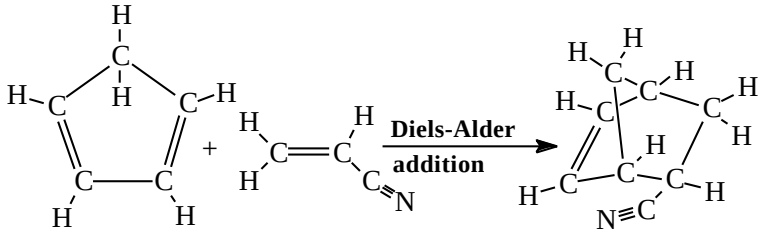
Although it does not truly dissolve hydrophobic organic substances, but may hold them in suspension as finely divided colloidal matter, water can often be used in place of organic solvents as a medium for organic reactions and for other applications. In addition to its not dissolving organic substances, water suffers from the disadvantage of reacting strongly with some reagents, such as $AlCl_3$ used in Friedel-Crafts reactions, strongly reducing $LiAlH_4$, and metallic sodium used in some applications. On the other hand, precisely because water is such a poor solvent for organic substances—the **hydrophobic effect**—some organic reactions proceed better in a water medium. Water is an excellent solvent for some of the more hydrophilic biological molecules, such as glucose, that are gaining favor as reactants for green chemical processes.

Table 20.1 Solvents for Which Substitutes Have Been Developed

Solvent	Disadvantages of solvent	Substitute	Characteristics of subsitute
Benzene	Toxic, causing blood disorders and suspected of causing leukemia, metabolized to toxic phenol	Toluene	Much less toxic than benzene because of the presence of a metabolically oxidizable methyl substituent group; produces hippuric acid metabolite
n-Hexane	Neurotoxic causing peripheral neuropathy manifested by mobility loss, reduced sensations in extremeties	2,5-Dimethylhexane	Lacks toxicity characteristics of *n*-hexane, significantly higher boiling point may be a disadvantage
Glycol ethers	Ethylene glycol monomethyl ether and ethylene glycol monoethyl ether have adverse reproductive and developmental effects in animals	1-Methoxy-2-propanol	Less toxic than the glycol ethers, but still effective as a solvent
Various organic solvents	Flammability, toxicity, poor biodegradability, tendency to contribute to photochemical smog	Supercritical fluid carbon dioxide	Widely available, good solvent for organic solutes, readily removed by evaporation, nonpolluting, except as a greenhouse gas if allowed to escape

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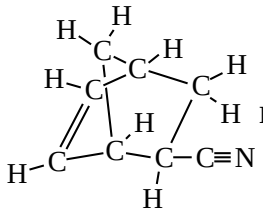
An interesting reaction attributed to the hydrophobic effect is illustrated by the following Diels-Alder addition reaction carried out with the poorly water-soluble reactants held as a suspension in water:[8]



Cyclopentadiene Acrylonitrile

(20.7.1)

It is believed that the reaction actually occurs in water, and the water-insoluble product comes out of the water as an organic phase. A significant aspect of the reaction is that the Diels-Alder addition product is in the endo form as opposed to the exo form shown below:



Exo form of adduct

The preferential formation of the endo form is attributed to so-called better hydrophobic packing and consequent less exposure to solvent water for the transition state leading to the endo form. In general, for reactions of the type described above, the reactants existing separately in water have a higher energy than they would in the more "friendly" surroundings of an organic solvent. The transition state between two hydrophobic reactants in water has less exposure to the "hostile" water environment than do the two reactants separately. This energetically favored transition state leads to a more facile reaction in water and favors products in which exposure to water is minimized.

In cases where the hydrophobic effect of water as described above is excessive, it is possible to reduce it by adding organic cosolvents. One solvent that is useful for this purpose is ethanol. Ethanol has the additional advantage of being readily prepared from biological sources and being degradable. Therefore, it, too, largely meets the criteria of a "green" solvent.

Largely ignored during the development of organic synthesis, water is getting renewed attention as a medium for organic chemical reactions and processes. This is due largely to water's being the ultimate green solvent with no detrimental environmental, safety (flammability), or toxicological aspects to its use. As the price for feedstocks for making organic solvents has increased—an especially painful phenomenon with rising petroleum prices in year 2000—the fact that water is essentially free increases its attractiveness. Water is a good solvent for many biological materials gaining favor as green chemistry reagents, and, as discussed above, its repulsion of some organophilic reagents can be advantageous in some

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cases. Water-insoluble organic products are readily separated from water without having to distill off an organic solvent. The control of heat and temperature is an important aspect of many chemical processes. For heat and temperature control, water is the best solvent to use because of its very high heat capacity (see Chapter 11, Table 11.1).

Dense Phase Carbon Dioxide as a Solvent

Substances that are normally considered to be gases take on special properties when highly compressed. The general diagram shown in Figure 20.3 shows that, at temperatures exceeding a critical temperature, T_C, and pressures exceeding a critical pressure, P_C, the distinction between liquid and gas disappears and a substance becomes a **supercritical fluid**. The most widely studied supercritical fluid is that formed by carbon dioxide, for which T_C is 31.1˚C and P_C is 73.8 atm. Supercritical fluids have many useful solvent properties. It has also been found, however, that highly compressed carbon dioxide below the critical point, where it is not supercritical, but may exist as a mixture of liquid and gas, has some excellent solvent properties as well. The term **dense phase fluid** is used to designate a highly compressed, dense substance that may be a supercritical fluid, highly compressed gas, or mixture of gas and liquid.[9]

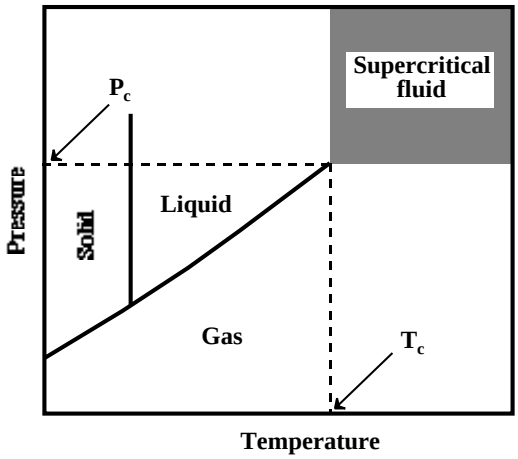


Figure 20.3 Temperature-pressure plot showing supercriticality.

Dense phase fluids have a number of interesting solvent properties and have been extensively investigated as extractants and for chromatographic separations (supercritical fluid chromatography). An important characteristic of these fluids is their much lower viscosities than conventional liquids; that of supercritical CO_2 is only about 1/30 the viscosity of liquids normally used as solvents. This means that solutes diffuse much more readily in supercritical fluids, thus enabling them to react much faster. The wide latitude within which pressures and temperatures of dense phase fluids may be changed enables their properties to be varied widely.

Supercritical fluid carbon dioxide is an excellent solvent for organic solutes. This has led to its uses in place of organochlorine solvents for cleaning metal parts and in dry cleaning. A major advantage of supercritical fluid carbon dioxide in some

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applications is that it is readily evaporated from solutes by releasing pressure. This has led to interest in the solvent as a vehicle for paints and coatings. With the appropriate apparatus, the released carbon dioxide can be reclaimed and recompressed back to a supercritical state for recycling. This capability tends to overcome criticism of the use of carbon dioxide, which is, of course, a greenhouse gas when released to the atmosphere. Supercritical fluid carbon dioxide has a highly organophilic nature, which may be excessive for some applications with more polar or ionic solutes. Addition of polar cosolvents, such as methyl alcohol, can overcome this disadvantage. A further advantage of supercritical fluid carbon dioxide as a solvent is its ability to dissolve gases, enhanced by the very high pressure under which supercritical fluid carbon dioxide must be maintained. This enables reactions to occur efficiently with gaseous reactants in supercritical fluid carbon dioxide that would otherwise not be possible.

Supercritical fluids have some disadvantages. The major disadvantage of such solvents is the special apparatus required to maintain supercritical conditions. However, supercritical fluid carbon dioxide's advantages of low cost, high abundance from a number of sources, nontoxic nature, nonflammability, and the fact that it is not classified as a volatile organic solvent (VOC) will undoubtedly lead to increased uses of this solvent in the future.

20.8 SYNTHETIC AND PROCESSING PATHWAYS

From the standpoint of green chemistry, the ideal chemical synthesis begins with a readily available, inexpensive, nontoxic material and converts it by one step with 100% yield and 100% atom efficiency to the desired product. Although such a totally efficient synthesis almost never can be realized, it does provide a framework within which to attempt to produce the desired product using the least possible reagent and reaction media (solvent) by the most straightforward possible pathway. When this is done, pollution is minimized at its source and the objectives of the practice of green chemistry are fulfilled.

In evaluating the degree to which synthetic and processing pathways are consistent with the practice of green chemistry, it is useful to consider three major categories of synthetic reactions, recognizing that two or even all three may be involved in making a desired product:

- **Addition reactions** in which all reagents are incorporated into product
- **Substitution reactions** in which a reagent or parts of it replace groups on another reagent
- **Elimination reactions** in which substances are eliminated from the feedstock as byproducts

Where they can be used, addition reactions are best because all starting materials end up in product, and there is no byproduct for which disposal or finding another use is required. By their nature, substitution reactions generate at least some byproducts. Elimination reactions do not require input of materials other than feedstocks, but do generate byproducts requiring disposal or recycling.

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20.9 THE ROLE OF CATALYSTS

In some cases, catalysts tend to add to the hazards of chemical processes and to produce troublesome byproducts and product contaminants. This can occur, for example, with homogeneous catalysts that are intimately mixed with the reagents involved in chemical synthesis. Catalysts that are most amenable to the practice of green chemistry are heterogeneous catalysts, such as molecular sieves, that can be kept entirely separate from products. Insofar as possible, such catalysts should be nontoxic.

Although they do not involve catalysts in the strictest sense, alternatives to chemical or heat energy for the introduction of energy required to carry out a chemical process can produce a much more environmentally attractive process. The two main ways of doing this are through the use of electricity or of photochemical energy.

The passage of a direct current of electricity through a reaction medium can cause both reductions and oxidations to occur. Reduction, the addition of electrons, e^-, can occur at the relatively negatively charged cathode, and oxidation, the loss of electrons, at the relatively positively charged anode. A simple example of an electrochemical process used to manufacture industrial chemicals occurs when a direct current is passed through molten sodium chloride, NaCl. At the cathode, sodium ion is reduced,

$$Na^+ + e^- \rightarrow Na(l) \qquad (20.9.1)$$

and at the anode, chloride ion is oxidized to elemental chlorine gas,

$$2Cl^- \rightarrow Cl_2(g) + 2e^- \qquad (20.9.2)$$

giving the following net reaction:

$$2Na^+ + 2Cl^- \rightarrow 2Na(l) + Cl_2(g) \qquad (20.9.3)$$

The reaction utilizes electrical energy efficiently and occurs with 100% atom economy.

Electrochemical oxidation and reduction can be controlled by the potentials applied, by the media in which they occur, and by the electrodes used. In a sense, electrochemical processes use “matter-free” reagents; no other approach comes any closer to the attainment of ideal green chemistry.

Enzymatically catalyzed reactions carried out by genetically engineered microorganisms can be combined with electrochemical processes to give very clean and efficient syntheses in some cases. An example of such a synthesis is that of corduritol C, for which the reaction scheme is shown in Figure 20.4.[10] In this case, the starting material shown by the first structure in Figure 20.4 was made enzymatically by the action of *Escherichia coli* pDTG601 bacteria. The rest of the reaction scheme consists of electrochemical reactions and hydrolysis reactions.

Photochemical reactions use the energy of photons of light or ultraviolet radiation to cause reactions to occur. For electromagnetic radiation of frequency ν, the energy of a photon is given by the equation $E = h\nu$, where h is Planck’s constant.

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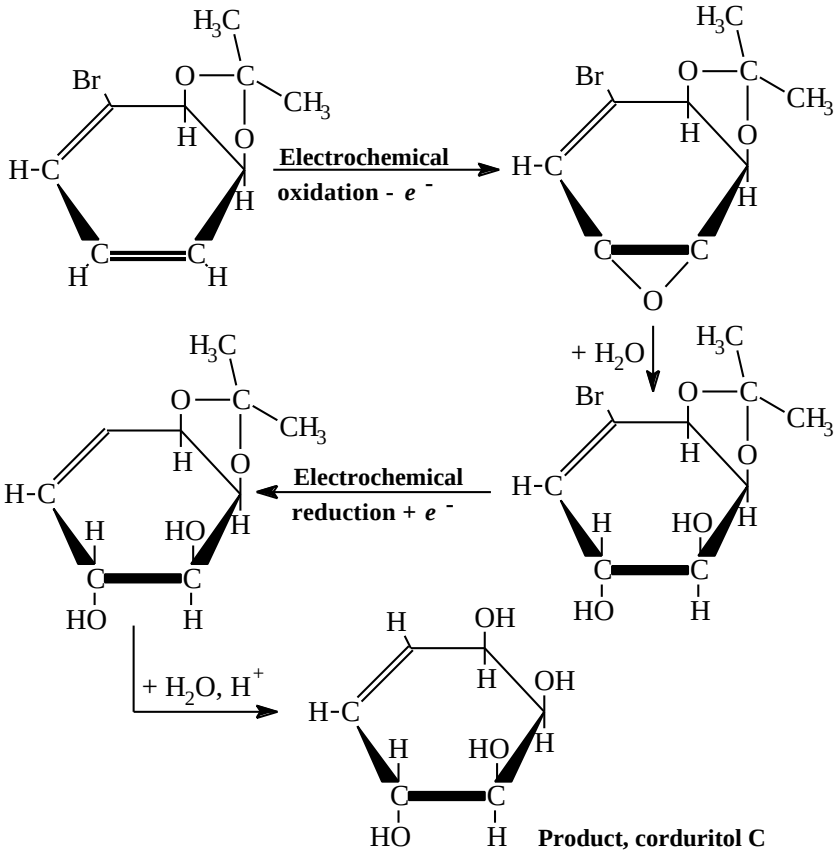
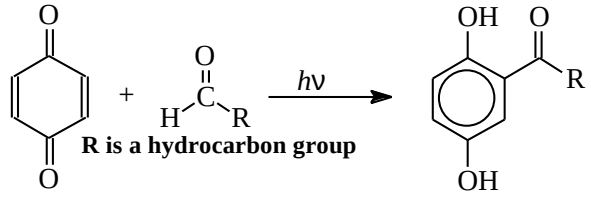


Figure 20.4 Use of electrochemical processes in the synthesis of corduritol C.

There is a significant potential to use photochemical energy to cause synthesis reactions to occur more efficiently and with less production of waste byproducts than nonphotochemical processes.[11] One example is the acylation of benzoquinone with an aldehyde to produce an acylhydroquinone, an intermediate used to make some specialty polymers:



(20.9.4)

This reaction occurs with 100 % atom economy. Unlike the standard Friedel-Crafts type of reaction, which utilize the catalytic effect of Lewis acid-type acidic halides, particularly aluminum chloride, $AlCl_3$, the photochemical process does not require moisture- and air-sensitive, potentially reactive catalytic substances.

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20.10 BIOLOGICAL ALTERNATIVES

Organically bound carbon is the basic building block of the world's vast organic chemical and polymer industries. At the present time, virtually all of this carbon is provided by petroleum and natural gas. Although these sources are vast and can supply needed carbon for many decades, particularly if alternatives to their use for fuel are developed, they are depletable resources and ultimately nonsustainable. A renewable, sustainable alternative is provided by photosynthetically produced biomass. Biomass consists largely of biopolymeric cellulose, hemicellulose, starch, lignin, and protein, all with the potential to be used directly or after chemical or biochemical modification. In addition, biological processes produce a variety of monomers, including sugars (glucose, sucrose), oils and fats (triglycerides), waxes, amino acids, and substances extractable from plants, such as hydrocarbon terpenes. It has been estimated that biological sources of these materials could supply essentially all U. S., and presumably world, needs for fixed carbon chemical feedstocks.[12] Much of the research effort at the U.S. National Renewable Energy Laboratory in Golden, Colorado is devoted to the development of cost-effective practical methodologies for the selective conversion of biological polymers and monomers to useful chemicals and chemical feedstocks.

Biological waste materials constitute much of the solid waste for which disposal is required. One attractive alternative is the use of much of this solid waste as a raw material, or food source, in the biological synthesis of desired chemical feedstocks.

An attractive feature of biological systems is the enzyme-mediated reactions that they carry out under very mild ambient conditions. The industrial Haber process for the synthesis of ammonia from elemental hydrogen and nitrogen,

$$3H_2 + N_2 \rightarrow 2NH_3 \qquad (20.10.1)$$

is carried out over a catalyst under extreme conditions of 500°C temperature and 200 atmospheres (atm) pressure. Bacteria, such as the nitrogen-fixing *Rhizobium* bacteria on the roots of leguminous plants use enzymes to fix atmospheric nitrogen at soil temperatures of 25°C or less and atmospheric pressure.

In industrial chemical processes, oxidation is frequently carried out by a variety of oxidants using a wide range of catalysts. Many of the oxidants, such as dichromate or ozone, as well as many of the catalysts, pose hazards of high reactivity and toxicity. Natural systems, in contrast, carry out all the oxidations required by using molecular oxygen, O_2, and hydrogen peroxide, H_2O_2. In so doing, organisms use elegant reaction schemes employing enzymes as catalysts. These enzymes include mono-oxygenases to catalyze oxidation by O_2 and peroxidases to catalyze oxidations with hydrogen peroxide.

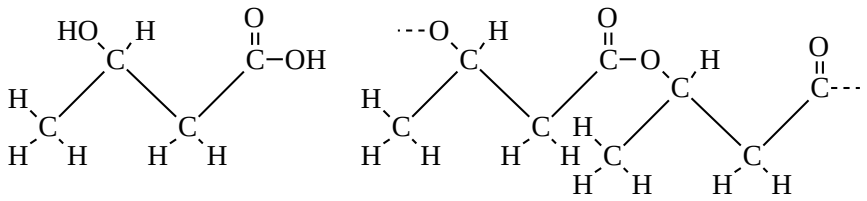
Biopolymers

The manufacture of synthetic polymers consumes large quantities of petroleum for raw material, and synthetic and natural polymers make up a large fraction of solid waste. For these reasons, it is desirable to both make polymers from renewable biological sources and to synthesize and use polymers that will biodegrade after disposal. Nature has provided a large variety of polymer factories, producing useful

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polymers such as cellulose in wood and cotton, lignin in wood, and protein in wool and silk. With the exception of degradation-resistant lignin, these polymers, made by organisms, are also degradable by organisms, particularly fungi and bacteria. Synthetic polymers can be tailored for biodegradability. One approach that has been tried widely is to synthesize biodegradable polymers with modified starch. Other possibilities for the preparation of biodegradable polymers is to synthesize them from biodegradable monomers, including polylactic acid, polyvinyl alcohol, polyesters, cellulose acetate, and poly{3-hydroxybutyrate-3-hydroxyvalerate}.

Aside from the natural polymers that have long been known and used, such as cotton, the most active current area of research in natural polymers involves the poly(hydroxyalkanoate) esters (alkanoates). These polymers were found to be produced by fluorescent *Pseudomonads* and other bacteria,[13] which generate and store them as reserves of carbon and energy. Their production has now been achieved in transgenic (genetically engineered) plants.[14] The first of the biologically produced poly(hydroxyalkanoate) esters to be identified was a polymer of 3-hydroxybutyric acid (Figure 20.5). Numerous other hydroxyacids synthesized by microorganisms can be used to make these esters. It is possible to make poly(hydroxyalkanoate) ester polymers ranging in properties from flexible, stretchable elastomers and rubbery polymers to stiff, brittle solid plastics. In addition to their being biosynthesized without the need of petroleum-based monomers, the alkanoates reflect their biological origins in being completely biodegradable.



3-Hydroxybutyric acid Repeating unit of poly(3-hydroxybutyrate) polymer

Figure 20.5 A common hydroxy acid monomer, 3-hydroxybutyric acid, and representation of a polymer formed from this class of compound.

Clearly, the alkanoate ester polymers are “green” chemicals, and there is a great deal of interest in using them as commercial polymers. Although these polymers have been made on a small industrial scale by bacterial fermentation using plant-derived glucose as a substrate, this pathway may be too costly for commercial production. Production by plants is an attractive alternative, and some success has been achieved in so doing with plants genetically engineered with bacterial genes for alkanoate ester production. Genes from the bacterium *Alcaligenes eutrophus* have been added to *Arabidopsis thaliana*, to produce a genetically engineered plant that subsequently produced up to 14% dry mass of poly(hydroxybutyric acid) in its leaves. Alkanoate polymers and copolymers with varying chain lengths—hence, variable properties—have now been produced by plants. For example, genetically engineered *Arabidopsis* and *Brassica* have been shown to generate a copolyester of 3-hydroxybutyrate and 3-hydroxyvalerate.

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A potential concern with the hydroxybutyrates has to do with the use of one member of the series as an illicit drug. So-called gamma-butyrate, 4-hydroxybutyric acid, is the infamous "date-rape" drug, which has caused fatalities to victims who have ingested it with "spiked" drinks.

20.11 APPLICATIONS OF GREEN CHEMISTRY

The principles of green chemistry are being more widely applied in industry to reduce emissions and save money and materials. Significant success in this area has been achieved at Dow Chemical's manufacturing complex in Midland, Michigan.[15] This vast operation makes more than 500 products, including polymers, packaging, pesticides, and drugs. Although a strong effort had been made to reduce emissions for many years, in the mid-to-late-1990s a program was undertaken to further reduce production and emission of undesirable byproducts.

As is normally the case with efforts of this kind, substantial waste reductions were achieved by simple measures. One of these was the reduction by 15,500 kg/year of organochlorine compound emissions from the manufacture of Saran plastic by transferring product to a storage tank twice a day instead of only once. When only one transfer per day was performed, the tank was filled to capacity with liquid and vaporized organochlorine compound emissions had to be vented to waste. Retaining these materials for recycle from the half-filled tanks saved the company an estimated $34,000 per year.

The production of formaldehyde-containing tar wastes from resin manufacture was curtailed by switching catalysts and making processing changes. The cost of making these changes was $330,000, but they are estimated to save the company $3.3 million each year in waste-treatment costs. Improved recovery of unreacted reagent in the production of 2,4-D herbicide resulted in a 66% reduction in tetrachloroethylene wastes. Previous procedures in the manufacture of SB latex binder in paint were carried out so that wastes that required incineration because of hazardous impurities were mixed with recyclable wastes, thus requiring that the whole mixture be incinerated. Changing that practice to keep the recyclable wastes segregated enabled a higher degree of recycling, reducing butadiene and styrene wastes by 35%. A problem with butadiene used to make resins and rubber is that it forms butadiene dimer during storage. Butadiene dimer is an unusable material that requires disposal. Formation and deposition of the dimer in apparatus tends to clog equipment. Refrigeration of butadiene from the supplier was found to lower the rate of dimer formation and to significantly reduce wastes requiring disposal from this source. Reduction of wastes and pollutants released was achieved in the manufacture of Ethocel, a product with diverse applications as a stabilizing agent and binder in foods, drugs, and other materials. Use of a steam system to purge volatile substances from the product along with a refrigerated condenser to the system used to recover volatile substances reduced both wastes and pollutants released in the form of chloroethane and toluene by between 50 % and 60 %.

The success of Dow's "green chemistry" initiative at Midland, though modest in terms of cost savings relative to the annual budget of the complex, has provided impetus for additional initiatives of a similar nature in the company. Similar measures are planned for the company's large petrochemical manufacturing operation in Freeport, Texas. In addition, the company has set a goal of reducing toxic chemicals

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emissions by 50 to 90 % over the decade ending in 2005. Similar initiatives are ongoing, with other companies raising the prospect of much lower chemical emissions in the future.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

Laws that have emphasized dealing with environmental problems after they have occurred represent a [1]_____ approach. Green chemistry can be defined as [2]_____

_____.
Green chemistry is [3]_____ because it is less costly, makes efficient use of raw materials, and does not cause an intolerable accumulation of hazardous-waste products. Two often complementary approaches to the practice of green chemistry are [4]_____

_____.
The equation

$$\frac{\text{Molecular mass of desired product}}{\text{Total molecular mass of materials generated}}$$

defines [5]_____. The ultimate in the parameter just defined is achieved when [6]_____. The practice of avoiding use or production of flammable, reactive, explosive, or toxic substances occurs under the category of [7]_____. Some attributes of a feedstock consistent with the practice of green chemistry are [8]_____

_____.
In a generalized sense, the overall process of obtaining a useful product from a feedstock, such as petroleum or biological materials, may be divided into the three categories of [9]_____
_____.
Biopolymers from plants that have the potential for use as biological feedstocks include [10]_____.
In some cases, an advantage of biological feedstocks is their high [11]_____ content. In some cases, a disadvantage of biological feedstocks is the [12]_____ of biomolecules. Probably the most important biological raw materials for chemical synthesis are [13]_____ produced by plants, [14]_____
_____. In addition to cellulose, a very abundant material in wood is [15]_____. A feedstock used to make a wide range of pharmaceutical chemicals, pesticides, antioxidants, and other chemical feedstocks

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that can now be synthesized biologically from glucose is [16]_____. Another feedstock used to make nylon 6,6 that potentially can be synthesized biologically is[17] _____. Two important factors driving reagent selection are [18]_____. The fact that certain structures or functional groups tend to create particular kinds of hazards is taken into account by considering [19]_____. In evaluating the safety of reagents and choosing safer alternatives, special attention should be given to [20]_____ consisting of particular groupings of atoms. A process in chemical synthesis that uses reagents such as permanganate (MnO_4^-), chromium(VI) compounds, osmium tetroxide, or *m*-chloroperbenzoic is[21]_____ _____, whereas a process using $LiAlH_4$ is[22]_____. Attachment of a methyl group in chemical synthesis is part of the more general process of [23]_____. A safer substitute for dimethyl sulfate in methylation reactions is [24]_____. The byproducts of this methylation reagent are [25]_____. The matrix in which or on which chemical processes occur is referred to as [26]_____ of which the most common type consists of [27]_____. The interaction of solvent molecules with solute molecules is referred to as [28]_____. A solvent that causes lipid peroxidation in the body is[29] _____ whereas volatile C_5-C_7 can cause [30]_____. A solvent used to enable application of dissolved or suspended dyes and other agents in formulations of paints, coatings, inks, and related materials is known as a [31]_____. A solvent used as a substitute for toxic benzene is [32]_____. The "greenest solvent" is [33]_____ _____. An effect of water solvent that occurs by repulsion of reactants or intermediates by water is the [34]_____. The control of heat and temperature in chemical reactions is aided in water because of water's [35]_____ _____. Carbon dioxide at a temperature above its critical temperature and a pressure above its critical pressure is a [36]_____. An important charcteristic of dense phase fluids, including supercritical fluids is their very low [37]_____ compared with normal liquids. A major advantage of supercritical fluid carbon dioxide in some applications is that it is [38]_____ _____ by releasing pressure. The major disadvantage of supercritical fluid solvents is [39]_____ _____. Three major categories of synthetic reactions are [40]_____ _____ of which the best type from the standpoint of green chemistry is [41]_____. Catalysts that are most amenable to the practice of green chemistry are [42]_____ _____ because they [43]_____ _____. Two alternatives to heat for introducing energy into a reaction scheme are [44]_____. The passage of a direct current of electricity through a reaction medium can cause both [45]_____ to occur. The three factors by which electrochemical oxidation and reduction can be controlled are [46]_____ _____. Photochemical reactions use the energy of [47]_____ to cause reactions to occur. An attractive feature of biological systems for performing chemical process is that enzyme-mediated reactions occur under [48]_____

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_____ conditions. Natural systems carry out all the oxidations required by using relatively benign [49]_____. Aside from the natural polymers, such as cellulose in cotton, that have been long known and used, the most active current area of research in natural polymers involves the [50]_____. The first of these to be identified were polymers of [51]_____.

Answers to Chapter Summary

1. command and control
2. the sustainable exercise of chemical science and technology within the framework of good practice of industrial ecology such that the use and handling of hazardous substances are minimized and such substances are never released to the environment
3. sustainable
4. use existing chemicals, but make them by environmentally benign syntheses and substitute chemicals made by environmentally benign syntheses for existing chemicals
5. atom economy
6. there is no byproduct
7. hazard reduction
8. place minimal demands on Earth's resources, safe as possible, acquisition and refining should be safe, and renewable.
9. source identification and acquisition, separation of desired components from source, and conversion of isolated feedstock to desired product
10. cellulose, hemicellulose, starch, lignin, and proteins
11. oxygen
12. complexity
13. carbohydrates
14. including glucose, fructose, sucrose, and starch
15. lignin
16. catechol
17. adipic acid
18. product selectivity and product yield
19. structure-activity relationships
20. functional groups
21. oxidation
22. reduction
23. alkylation
24. dimethyl carbonate
25. carbon dioxide and methanol
26. media
27. solvents
28. solvation
29. carbon tetrachloride
30. peripheral neuropathy
31. vehicle

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32. toluene
33. water
34. hydrophobic effect
35. very high heat capacity
36. supercritical fluid
37. viscosities
38. readily evaporated from solutes
39. the special apparatus required to maintain supercritical conditions
40. addition reactions, substitution reactions, and elimination reactions
41. addition reactions
42. heterogeneous catalysts
43. can be kept entirely separate from products
44. electrical energy and photochemical energy
45. reductions and oxidations
46. by the potentials applied, by the media in which they occur, and by the electrodes used
47. photons of light or ultraviolet radiation
48. very mild ambient
49. molecular oxygen and hydrogen peroxide
50. poly(hydroxyalkanoate) esters (alkanoates)
51. 3-hydroxybutyric acid

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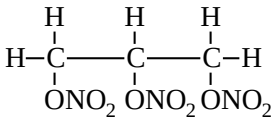
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QUESTIONS AND PROBLEMS

1. What are four categories of hazardous substances based on chemical properties? Which important class of hazardous substances does this classification scheme omit?
2. What is the practice of relating chemical formulas to toxicity?
3. What are three major categories of hazardous substances that are candidates for reduction in the practice of green chemistry?
4. Compare the preparation of a polymeric plastic or rubber from petroleum feed-stock with the production of poly(hydroxalkanoate) ester polymers from biological sources in terms of the three major steps in obtaining a feedstock and converting it to a useful product shown in Figure 20.1.

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5. Although abundant, why is lignin not a good candidate as a raw material?
6. In addition to its uses as a feedstock, what is a potential application of 3-dehydroshikimic acid?
7. Compare the roles of product selectivity and product yield in reagent selectivity for green chemistry.
8. What structural features of the compound,



 would make it hazardous? What is the nature of the hazard?
9. What is the potential use of dialkyl carbonates, such as dimethyl carbonate, in green chemical synthesis?
10. Calculate the atom economy of Reaction 20.5.3.
11. What are some uses of organic solvents other than for reaction media? What are some of the drawbacks of organic solvents for these uses?
12. In terms of interaction with reagents, what is the greatest disadvantage of water as a solvent? What is the greatest advantage of water as a solvent for a variety of solutes of biological origin?
13. What is a dense phase fluid? What form of dense phase carbon dioxide is produced at very high pressures and slightly elevated temperature?
14. How can water's hydrophobic effect be reduced? What is a "green" substance commonly used in lowering the hydrophobic effect?
15. What are the advantages of supercritical fluid carbon dioxide solvent? Why is carbon dioxide's volatility an advantage in some cases?
16. Why are polar cosolvents added to supercritical fluid carbon dioxide? What is a common polar cosolvent?
17. What are three major categories of synthetic reactions? Which of these is the most consistent with the practice of green chemistry? Why?
18. Discuss how electrons and photons can be regarded as catalysts. In what respects are they "massless" reagents?
19. Discuss and compare the conditions and relative advantages and disadvantages of the Haber process and its biological alternatives.
20. What are two major related advantages of bioipolymers in the practice of green chemistry? What are some of the most common biopolymers?
21. What is a common type of biopolymer synthesized by some kinds of bacteria and now by genetically engineered plants?

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22. List some of the applications of green chemistry that have actually been applied on an industrial scale.
23. Suggest how refrigeration of apparatus and storage tanks can aid green chemistry in industry. Are there any potential disadvantages to refrigeration?
24. What is the relationship of industrial ecology to green chemistry? In which ways are industrial ecology and green chemistry complementary?
25. What is the meaning of "command and control?" What are its limitations in the control of pollution?
26. In what sense does the practice of green chemistry ensure environmental quality by "natural," self-regulating means?
27. What is the role of sustainability in the practice of green chemistry?
28. How is atom economy defined? In what sense is it a key aspect of the practice of green chemistry?

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Manhan, Stanley E. "NATURE, SOURCES, AND ENVIRONMENTAL CHEMISTRY OF HAZARDOUS WASTES"
Fundamentals of Environmental Chemistry
Boca raton: LLC, CRC press, 2001

21 NATURE, SOURCES, AND ENVIRONMENTAL CHEMISTRY OF HAZARDOUS WASTES

21.1 INTRODUCTION

A **hazardous substance** is a material that may pose a danger to living organisms, materials, structures, or the environment by explosion or fire hazards, corrosion, toxicity to organisms, or other detrimental effects. What, then, is a hazardous waste? Although it has has been stated that,[1] "The discussion on this question is as long as it is fruitless," a simple definition of a **hazardous waste** is that it is a hazardous substance that has been discarded, abandoned, neglected, released or designated as a waste material, or one that might interact with other substances to be hazardous. The definition of hazardous waste is addressed in greater detail in Section 21.2, but, in a simple sense, it is a material that has been left where it should not be and that could cause harm to living creatures or its surroundings.

History of Hazardous Substances

Humans have always been exposed to hazardous substances, going back to prehistoric times when people inhaled noxious volcanic gases or succumbed to carbon monoxide from inadequately vented fires in cave dwellings sealed too well against Ice-Age cold. Slaves in Ancient Greece developed lung disease from weaving mineral asbestos fibers into cloth to make it more degradation-resistant. Some archaeological and historical studies have concluded that lead wine containers were a leading cause of lead poisoning in the more affluent ruling class of the Roman Empire, leading to erratic behavior such as fixation on spectacular sporting events, chronic unmanageable budget deficits, speculative purchases of overvalued stock, illicit trysts in governmental offices, and ill-conceived, overly ambitious military ventures in remote foreign lands. Alchemists who worked during the Middle Ages often suffered debilitating injuries and illnesses resulting from the hazards of their explosive and toxic chemicals. During the 1700s, runoff from mine-spoils piles

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began to create serious contamination problems in Europe. As the production of dyes and other organic chemicals developed from the coal tar industry in Germany during the 1800s, pollution and poisoning from coal tar byproducts was observed. By around 1900 the quantity and variety of chemical wastes produced each year was increasing sharply with the addition of wastes such as spent steel and iron pickling liquor, lead battery wastes, chromic wastes, petroleum refinery wastes, radium wastes, and fluoride wastes from aluminum ore refining. As the century progressed into the World War II era, the wastes and hazardous byproducts of manufacturing increased markedly from sources such as chlorinated solvent manufacture, pesticide synthesis, polymer manufacture, plastics, paints, and wood preservatives.

The Love Canal affair of the 1970s and 1980s brought hazardous wastes to public attention as a major political issue in the U.S. Starting around 1940, this site in Niagara Falls, New York, had received about 20,000 metric tons of chemical wastes containing at least 80 different chemicals. By 1994, state and federal governments had spent well over $100 million to clean up the site and relocate residents.

Other areas containing hazardous wastes that received attention included an industrial site in Woburn, Massachusetts, that had been contaminated by wastes from tanneries, glue-making factories, and chemical companies dating back to about 1850; the Stringfellow Acid Pits near Riverside, California; the Valley of the Drums in Kentucky; and Times Beach, Missouri, an entire town that was abandoned because of contamination by TCDD (dioxin).

The problem of hazardous wastes is truly international in scope.[2] As the result of the problem of dumping such wastes in developing countries, the 1989 Basel Convention on the Control of Transboundary Movement of Hazardous Wastes and their Disposal was held in Basel, Switzerland in 1989, and by 1998 had been signed by more than 100 countries. This treaty defines a long List A of hazardous wastes, a List B of nonhazardous wastes, and a List C of as yet unclassified materials. An example of a material on List C is polyvinyl chloride (PVC) coated wire, which is harmless itself, but may release dioxins or heavy metals when thermally treated.

Legislation

Governments in a number of nations have passed legislation to deal with hazardous substances and wastes. In the U.S., such legislation has included the following:

- Toxic Substances Control Act of 1976
- Resource Conservation and Recovery Act (RCRA) of 1976 (amended and reauthorized by the Hazardous and Solid Wastes Amendments Act (HSWA) of 1984)
- Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980

RCRA legislation charged the U.S. Environmental Protection Agency (EPA) with protecting human health and the environment from improper management and

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disposal of hazardous wastes by issuing and enforcing regulations pertaining to such wastes. RCRA requires that hazardous wastes and their characteristics be listed and controlled from the time of their origin until their proper disposal or destruction. Regulations pertaining to firms generating and transporting hazardous wastes require that they keep detailed records, including reports on their activities and manifests to ensure proper tracking of hazardous wastes through transportation systems. Approved containers and labels must be used, and wastes can only be delivered to facilities approved for treatment, storage, and disposal. There are about 290 million tons of wastes regulated by RCRA. In the U.S., about 3,000 facilities are involved in the treatment, storage, or disposal of RCRA wastes.

CERCLA (Superfund) legislation deals with actual or potential releases of hazardous materials that have the potential to endanger people or the surrounding environment at uncontrolled or abandoned hazardous-waste sites in the U.S. The act requires responsible parties or the government to clean up waste sites. Among CERCLA's major purposes are the following:

- Site identification
- Evaluation of danger from waste sites
- Evaluation of damages to natural resources
- Monitoring of release of hazardous substances from sites
- Removal or cleanup of wastes by responsible parties or government

CERCLA was extended for 5 years by the passage of the Superfund Amendments and Reauthorization Act (SARA) of 1986, legislation with greatly increased scope and additonal in funding. Actually longer than CERCLA, SARA encouraged the development of alternatives to land disposal that favor permanent solutions reducing volume, mobility, and toxicity of wastes; increased emphasis upon public health, research, training, and state and citizen involvement; and establishment of a new program for leaking underground (petroleum) storage tanks. After 1986 few new legislative initiatives dealing with hazardous wastes were forthcoming in the U.S. As of 1999, the U.S. Congress had gone for six years without reauthorizing Superfund. During 1999, both the House and Senate were considering passage of legislation to reauthorize the Superfund act in an amended form.[3]

As of 1998, there were 1,359 designated Superfund sites, of which 509 sites, 37 percent of the total, had been cleaned up at a total cost to companies of $15 billion.[4] Assuming the same cost for each of the remaining sites, an additional $25 billion in private-sector funds would be required to clean them up. The DuPont company, for example, listed an accrued liability of $561 million for waste-site cleanup on its 1997 annual report, down from $602 million in 1995.

21.2 CLASSIFICATION OF HAZARDOUS SUBSTANCES AND WASTES

Many specific chemicals in widespread use are hazardous because of their chemical reactivities, fire hazards, toxicities, and other properties. There are

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numerous kinds of hazardous substances, usually consisting of mixtures of specific chemicals. These include such things as explosives; flammable liquids; flammable solids, such as magnesium metal and sodium hydride; oxidizing materials such as peroxides; corrosive materials, such as strong acids; etiologic agents that cause disease; and radioactive materials.

Characteristics and Listed Wastes

For regulatory and legal purposes in the U.S., hazardous substances are listed specifically and are defined according to general characteristics. Under the authority of the Resource Conservation and Recovery Act (RCRA), the United States Environmental Protection Agency (EPA) defines hazardous substances in terms of the following **characteristics**:

- **Ignitability**, characteristic of substances that are liquids, the vapors of which are likely to ignite in the presence of ignition sources; nonliquids that may catch fire from friction or contact with water and that burn vigorously or persistently; ignitable compressed gases; and oxidizers
- **Corrosivity**, characteristic of substances that exhibit extremes of acidity or basicity or a tendency to corrode steel
- **Reactivity**, characteristic of substances that have a tendency to undergo violent chemical change (examples are explosives, pyrophoric materials, water-reactive substances, or cyanide- or sulfide-bearing wastes)
- **Toxicity**, defined in terms of a standard extraction procedure followed by chemical analysis for specific substances

In addition to classification by characteristics, EPA designates more than 450 **listed wastes** that are specific substances or classes of substances known to be hazardous. Each such substance is assigned an EPA **hazardous waste number** in the format of a letter followed by three numerals, where a different letter is assigned to substances from each of the four following lists:

- **F-type wastes from nonspecific sources**: For example, quenching wastewater treatment sludges from metal heat treating operations where cyanides are used in the process (F012).
- **K-type wastes from specific sources**: For example, heavy ends from the distillation of ethylene dichloride in ethylene dichloride production (K019).
- **P-type acute hazardous wastes**: Wastes that have been found to be fatal to humans in low doses, or capable of causing or significantly contributing to an increase in serious irreversible or incapacitating reversible illness. These are mostly specific chemical species such as fluorine (P056) or 3-chloropropane nitrile (P027).
- **U-Type miscellaneous hazardous wastes**: These are predominantly specific compounds such as calcium chromate (U032) or phthalic anhydride (U190).

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Compared with RCRA, CERCLA gives a rather broad definition of hazardous substances that includes the following:

- Any element, compound, mixture, solution, or substance, the release of which may substantially endanger public health, public welfare, or the environment
- Any element, compound, mixture, solution, or substance in reportable quantities designated by CERCLA Section 102
- Certain substances or toxic pollutants designated by the Federal Water Pollution Control Act
- Any hazardous air pollutant listed under Section 112 of the Clean Air Act
- Any imminently hazardous chemical substance or mixture that has been the subject of government action under Section 7 of the Toxic Substances Control Act (TSCA)
- With the exception of those suspended by Congress under the Solid Waste Disposal Act, any hazardous waste listed or having characteristics identified by RCRA § 3001

Hazardous Wastes

Three basic approaches to defining hazardous wastes are (1) a qualitative description by origin, type, and constituents; (2) classification by characteristics largely based upon testing procedures; and (3) by means of concentrations of specific hazardous substances. Wastes may be classified by general type such as "spent halogenated solvents," or by industrial sources such as "pickling liquor from steel manufacturing."

Hazardous Wastes and Air and Water Pollution Control

Somewhat paradoxically, measures taken to reduce air and water pollution (Figure 21.1) have had a tendency to increase production of hazardous wastes. Most water treatment processes yield sludges or concentrated liquors that require stabilization and disposal. Air scrubbing processes likewise produce sludges. Baghouses and precipitators used to control air pollution all yield significant quantities of solids, some of which are hazardous.

21.3 SOURCES OF WASTES

Quantities of hazardous wastes produced each year are not known with certainty and depend upon the definitions used for such materials. In 1988, the figure for RCRA-regulated wastes in the U.S. was placed at 290 million tons. However, most of this material was water, with only a few million tons consisting of solids. Some high-water-content wastes are generated directly by processes that require large quantities of water in waste treatment, and other aqueous wastes are produced by mixing hazardous wastes with wastewater.

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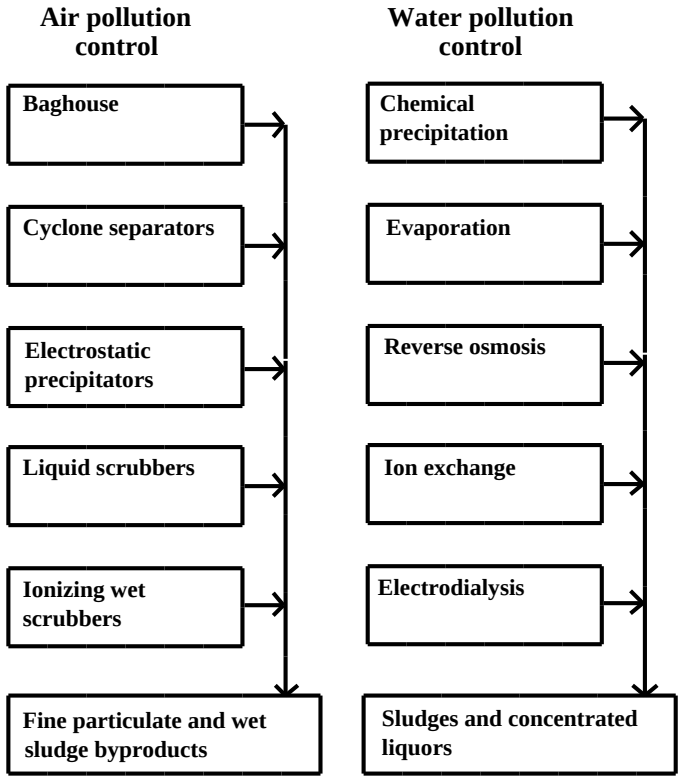


Figure 21.1 Potential contributions of air and water pollution control measures to hazardous wastes production.

Some wastes that might exhibit a degree of hazard are exempt from RCRA regulation by legislation. These exempt wastes include the following:

- Fuel ash and scrubber sludge from power generation by utilities
- Oil and gas drilling muds
- byproduct brine from petroleum production
- Cement kiln dust
- Waste and sludge from phosphate mining and beneficiation
- Mining wastes from uranium and other minerals
- Household wastes

Types of Hazardous Wastes

In terms of quantity by weight, the greatest quantities are those from categories designated by hazardous waste numbers preceded by F and K, respectively. The former are those from nonspecific sources and include the following examples:

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- F001—The spent halogenated solvents used in degreasing: tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and the chlorinated fluorocarbons; and sludges from the recovery of these solvents in degreasing operations
- F004—The spent nonhalogenated solvents: cresols, cresylic acid, and nitrobenzene; and still bottoms from the recovery of these solvents
- F007—Spent plating-bath solutions from electroplating operations
- F010—Quenching-bath sludge from oil baths from metal heat treating operations

The "K-type" hazardous wastes are those from specific sources produced by industries such as the manufacture of inorganic pigments, organic chemicals, pesticides, explosives, iron and steel, and nonferrous metals, and from processes such as petroleum refining or wood preservation; some examples are given below:

- K001—Bottoms sediment sludge from the treatment of wastewaters from wood-preserving processes that use creosote and/or pentachlorophenol
- K002—Wastewater treatment sludge from the production of chrome yellow and orange pigments
- K020—Heavy ends (residue) from the distillation of vinyl chloride in vinyl chloride monomer production
- K043—2,6-Dichlorophenol waste from the production of 2,4-D
- K047—Pink/red water from TNT operations
- K049—Slop oil emulsion solids from the petroleum refining industry
- K060—Ammonia lime still sludge from coking operations
- K067—Electrolytic anode slimes/sludges from primary zinc production

The remainder of wastes consist of reactive wastes, corrosive wastes, toxic wastes, ignitable wastes, and "P" wastes (discarded commercial chemical products, off-specification species, containers, and spill residues), "U" wastes, and unspecified types.

Hazardous-Waste Generators

Several hundred thousand companies generate hazardous wastes in the U. S., but most of these generators produce only small quantities. Hazardous waste generators are unevenly distributed geographically across the continental U. S., with a relatively large number located in the industrialized upper Midwest, including the states of Illinois, Indiana, Ohio, Michigan, and Wisconsin.

Industry types of hazardous-waste generators can be divided among the seven following major categories, each containing some of 10–20 % of hazardous waste

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generators: chemicals and allied products manufacture, petroleum-related industries, fabricated metals, metal-related products, electrical equipment manufacture, "all other manufacturing," and nonmanufacturing and nonspecified generators. About 10% of the generators produce more than 95% of all hazardous wastes. Whereas, as noted above, the number of hazardous-waste generators is distributed relatively evenly among several major types of industries, 70–85 % of the *quantities* of hazardous wastes are generated by the chemical and petroleum industries. Of the remainder, about 3/4 comes from metal-related industries, and about 1/4 from all other industries.

21.4 FLAMMABLE AND COMBUSTIBLE SUBSTANCES

Most chemicals that are likely to burn accidentally are liquids. Liquids form **vapors**, which are usually more dense than air, and thus tend to settle. The tendency of a liquid to ignite is measured by a test in which the liquid is heated and periodically exposed to a flame until the mixture of vapor and air ignites at the liquid's surface. The temperature at which ignition occurs under these conditions is called the **flash point**.

With these definitions in mind, it is possible to divide ignitable materials into four major classes. A **flammable solid** is one that can ignite from friction or from heat remaining from its manufacture, or that might cause a serious hazard if ignited. Explosive materials are not included in this classification. A **flammable liquid** is one having a flash point below 60.5˚C (141˚F). A **combustible liquid** has a flash point in excess of 60.5˚C, but below 93.3˚C (200˚F). Where gases are substances that exist entirely in the gaseous phase at 0˚C and 1 atm pressure, a **flammable compressed gas** meets specified criteria for lower flammability limit, flammability range (see below), and flame projection.

In considering the ignition of vapors, two important concepts are those of flammability limit and flammability range. Values of the vapor–air ratio below which ignition cannot occur because of insufficient fuel define the **lower flammability limit** (**LFL**). Similarly, values of the vapor–air ratio above which ignition cannot occur because of insufficient air define the **upper flammability limit** (**UFL**). The difference between upper and lower flammability limits at a specified temperature is the **flammability range**. Table 21.1 gives some examples of these values for common liquid chemicals. The percentage of flammable substance for best combustion (most explosive mixture) is labeled "optimal." In the case of acetone, for example, the optimal flammable mixture is 5.0% acetone.

One of the more disastrous problems that can occur with flammable liquids is a boiling liquid expanding vapor explosion, BLEVE. These are caused by rapid pressure buildup in closed containers of flammable liquids heated by an external source. The explosion occurs when the pressure buildup is sufficient to break the container walls.

Combustion of Finely Divided Particles

Finely divided particles of combustible materials are somewhat analogous to vapors with respect to flammability. One such example is a spray or mist of hydrocarbon liquid in which oxygen has the opportunity for intimate contact with the

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liquid particles causing the liquid to ignite at a temperature below its flash point.

Table 21.1 Flammabilities of Some Common Organic Liquids

Liquid	Flash point (˚C)[1]	Volume percent in air	
		LFL[2]	UFL[2]
Diethyl ether	-43	1.9	36
Pentane	-40	1.5	7.8
Acetone	-20	2.6	13
Toluene	4	1.27	7.1
Methanol	12	6.0	37
Gasoline (2,2,4-tri-methylpentane)	---	1.4	7.6
Naphthalene	157	0.9	5.9

[1] Closed-cup flash point test
[2] LFL, lower flammability limit; UFL, upper flammability limit at 25˚C.

Dust explosions can occur with a large variety of solids that have been ground to a finely divided state. Many metal dusts, particularly those of magnesium and its alloys, zirconium, titanium, and aluminum, can burn explosively in air. In the case of aluminum, for example, the reaction is the following:

$$4Al(powder) + 3O_2(from\ air) \rightarrow 2Al_2O_3 \quad (21.4.1)$$

Coal dust and grain dusts have caused many fatal fires and explosions in coal mines and grain elevators, respectively. Dusts of polymers such as cellulose acetate, polyethylene, and polystyrene can also be explosive.

Oxidizers

Combustible substances are reducing agents that react with **oxidizers** (oxidizing agents or oxidants) to produce heat. Diatomic oxygen, O_2, from air is the most common oxidizer. Many oxidizers are chemical compounds that contain oxygen in their formulas. The halogens (periodic table group 7A) and many of their compounds are oxidizers. Some examples of oxidizers are given in Table 21.2.

An example of a reaction of an oxidizer is that of concentrated HNO_3 with copper metal, which gives toxic NO_2 gas as a product:

$$4HNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2 \quad (21.4.2)$$

Spontaneous Ignition

Substances that catch fire spontaneously in air without an ignition source are called **pyrophoric**. These include several elements—white phosphorus, the alkali metals (group 1A), and powdered forms of magnesium, calcium, cobalt, manganese,

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Table 21.2 Examples of Some Oxidizers

Name	Formula	State of matter
Ammonium nitrate	NH_4NO_3	Solid
Ammonium perchlorate	NH_4ClO_4	Solid
Bromine	Br_2	Liquid
Chlorine	Cl_2	Gas (stored as liquid)
Fluorine	F_2	Gas
Hydrogen peroxide	H_2O_2	Solution in water
Nitric acid	HNO_3	Concentrated solution
Nitrous oxide	N_2O	Gas (stored as liquid)
Ozone	O_3	Gas
Perchloric acid	$HClO_4$	Concentrated solution
Potassium permanganate	$KMnO_4$	Solid
Sodium dichromate	$Na_2Cr_2O_7$	Solid

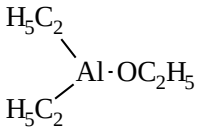
iron, zirconium, and aluminum. Also included are some organometallic compounds, such as ethyllithium (LiC_2H_5) and phenyllithium (LiC_6H_5), and some metal carbonyl compounds such as iron pentacarbonyl, $Fe(CO)_5$. Another major class of pyrophoric compounds consists of metal and metalloid hydrides, including lithium hydride, LiH; pentaborane, B_5H_9; and arsine, AsH_3. Moisture in air is often a factor in spontaneous ignition. For example, lithium hydride undergoes the following reaction with water from moist air:

$$LiH + H_2O \rightarrow LiOH + H_2 + \text{heat} \tag{21.4.4}$$

The heat generated from this reaction can be sufficient to ignite the hydride so that it burns in air:

$$2LiH + O_2 \rightarrow Li_2O + H_2O \tag{21.4.5}$$

Some compounds with organometallic character are also pyrophoric. An example of such a compound is diethylethoxyaluminum:



Diethylethoxyaluminum

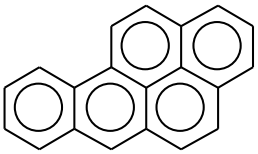
Many mixtures of oxidizers and oxidizable chemicals catch fire spontaneously and are called **hypergolic mixtures**. Nitric acid and phenol form such a mixture.

Toxic Products of Combustion

Some of the greater dangers of fires are from toxic products and byproducts of combustion. The most obvious of these is carbon monoxide, CO, which can cause

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serious illness or death because it forms carboxyhemoglobin with hemoglobin in the blood so that the blood no longer carries oxygen to body tissues. Toxic SO_2, P_4O_{10}, and HCl are formed by the combustion of sulfur, phosphorus, and organochlorine compounds, respectively. A large number of noxious organic compounds such as aldehydes are generated as byproducts of combustion. In addition to forming carbon monoxide, combustion under oxygen-deficient conditions produces polycyclic aromatic hydrocarbons consisting of fused ring structures. Some of these compounds, such as benzo[a]pyrene, below, are precarcinogens that are acted upon by enzymes in the body to yield cancer-producing metabolites.



Benzo(a)pyrene

21.5 REACTIVE SUBSTANCES

Reactive substances are those that tend to undergo rapid or violent reactions under certain conditions. Such substances include those that react violently or form potentially explosive mixtures with water. An example is sodium metal, which reacts strongly with water as follows:

$$2Na + 2H_2O \rightarrow 2NaOH + H_2 + \text{heat} \qquad (21.5.1)$$

This reaction usually generates enough heat to ignite the sodium and hydrogen. Explosives constitute another class of reactive substances. For regulatory purposes, substances that produce toxic gases or vapors when they react with water, acid, or base are also classified as reactive. Hydrogen sulfide or hydrogen cyanide are the most common toxic substances released in this manner.

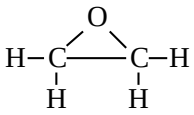
Heat and temperature are usually very important factors in reactivity. Many reactions require energy of activation to get them started. The rates of most reactions tend to increase sharply with increasing temperature and most chemical reactions give off heat. Therefore, once a reaction is started in a reactive mixture lacking an effective means of heat dissipation, the rate may increase exponentially with time, leading to an uncontrollable event. Other factors that may affect reaction rate include physical form of reactants (for example, a finely divided metal powder that reacts explosively with oxygen, whereas a single mass of metal barely reacts), rate and degree of mixing of reactants, degree of dilution with nonreactive media (solvent), presence of a catalyst, and pressure.

Some chemical compounds are self-reactive in that they contain oxidant and reductant in the same compound. Nitroglycerin, a strong explosive with the formula $C_3H_5(ONO_2)_3$ decomposes spontaneously to CO_2, H_2O, O_2, and N_2 with a rapid release of a very high amount of energy. Pure nitroglycerin has such a high inherent instability that the slightest blow might be sufficient to detonate it. Trinitrotoluene (TNT) is also an explosive with a high degree of reactivity. However, it is inherently relatively stable because some sort of detonating device is required to cause it to explode.

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Chemical Structure and Reactivity

As shown in Table 21.3, some chemical structures are associated with high reactivity. High reactivity in some organic compounds results from unsaturated bonds in the carbon skeleton, particularly where multiple bonds are adjacent (allenes, C=C=C) or separated by only one carbon–carbon single bond (dienes, C=C-C=C). Some organic structures involving oxygen are very reactive. Examples are oxiranes, such as ethylene oxide,



Ethylene oxide

hydroperoxides (ROOH), and peroxides (ROOR'), where R and R' stand for hydrocarbon moieties such as the methyl group, $-CH_3$. Many organic compounds containing nitrogen along with carbon and hydrogen are very reactive. Included are triazenes containing a functionality with three nitrogen atoms (R-N=N-N), some azo

Table 21.3 Examples of Reactive Compounds and Structures

Name	Structure or formula
Organic	
Allenes	C=C=C
Dienes	C=C−C=C
Azo compounds	C−N=N−C
Triazenes	C−N=N−N
Hydroperoxides	R−OOH
Peroxides	R−OO−R'
Alkyl nitrates	$R-O-NO_2$
Nitro compounds	$R-NO_2$
Inorganic	
Nitrous oxide	N_2O
Nitrogen halides	NCl_3, NI_3
Interhalogen compounds	BrCl
Halogen oxides	ClO_2
Halogen azides	ClN_3
Hypohalites	NaClO

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compounds (R-N=N-R'), and some nitriles in which a nitrogen atom is triply bonded to a carbon atom:

$$R-C\equiv N \qquad \textbf{Nitrile}$$

Functional groups containing both oxygen and nitrogen tend to impart reactivity to an organic compound. Examples of such functional groups are alkyl nitrates ($R–NO_2$), alkyl nitrites (R–O–N=O), nitroso compounds (R–N=O), and nitro compounds ($R–NO_2$).

Many different classes of inorganic compounds are reactive. These include some of the halogen compounds of nitrogen (shock-sensitive nitrogen triiodide, NI_3, is an outstanding example), compounds with metal-nitrogen bonds (NaN_3), halogen oxides (ClO_2), and compounds with oxyanions of the halogens. An example of the last group of compounds is ammonium perchlorate, NH_4ClO_4, which was involved in a series of massive explosions that destroyed 8 million lb of the compound and demolished a 40 million lb/year U.S. rocket fuel plant near Henderson, Nevada, in 1988. (By late 1989 a new $92 million plant for the manufacture of ammonium perchlorate had been constructed near Cedar City in a remote region of southwest Utah. Prudently, the buildings at the new plant have been placed at large distances from each other!)

Explosives such as nitroglycerin or TNT are single compounds containing both oxidizing and reducing functions in the same molecule. Such substances are commonly called **redox compounds**. Some redox compounds have even more oxygen than is needed for a complete reaction and are said to have a positive balance of oxygen, some have exactly the stoichiometric quantity of oxygen required (zero balance, maximum energy release), and others have a negative balance and require oxygen from outside sources to completely oxidize all components. Trinitrotoluene has a substantial negative balance of oxygen; ammonium dichromate ($(NH_4)_2Cr_2O_7$) has a zero balance, reacting with exact stoichiometry to H_2O, N_2, and Cr_2O_3; and treacherously explosive nitroglycerin has a positive balance, as shown by the following reaction:

$$4C_3H_5N_3O_9 \rightarrow 12CO_2 + 10H_2O + 6N_2 + O_2 \qquad (21.5.2)$$

21.6 CORROSIVE SUBSTANCES

Corrosive substances are regarded as those that dissolve metals or cause oxidized material to form on the surface of metals—rusted iron is a prime example—and, more broadly, cause deterioration of materials, including living tissue, that they contact.[5] Most corrosives belong to at least one of the four following chemical classes: (1) strong acids, (2) strong bases, (3) oxidants, (4) dehydrating agents. Table 21.4 lists some of the major corrosive substances and their effects.

Sulfuric Acid

Sulfuric acid is a prime example of a corrosive substance. As well as being a strong acid, concentrated sulfuric acid is also a dehydrating agent and oxidant. The tremendous affinity of H_2SO_4 for water is illustrated by the heat generated when water

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Table 21.4 Examples of Some Corrosive Substances

Name and formula	Properties and effects
Nitric acid, HNO_3	Strong acid and strong oxidizer, corrodes metal, reacts with protein in tissue to form yellow xanthoproteic acid, lesions are slow to heal
Hydrochloric acid, HCl	Strong acid, corrodes metals, gives off HCl gas vapor, which can damage respiratory tract tissue
Hydrofluoric acid, HF	Corrodes metals, dissolves glass, causes particularly bad burns to flesh
Alkali metal hydroxides, NaOH and KOH	Strong bases, corrode zinc, lead, and aluminum, substances that dissolve tissue and cause severe burns
Hydrogen peroxide, H_2O_2	Oxidizer, all but very dilute solutions cause severe burns
Interhalogen compounds such as ClF, BrF_3	Powerful corrosive irritants that acidify, oxidize, and dehydrate tissue
Halogen oxides such as OF_2, Cl_2O, Cl_2O_7	Powerful corrosive irritants that acidify, oxidize, and dehydrate tissue
Elemental fluorine, chlorine, bromine (F_2, Cl_2, Br_2,)	Very corrosive to mucous membranes and moist tissue, strong irritants

and concentrated sulfuric acid are mixed. If this is done incorrectly by adding water to the acid, localized boiling and spattering can occur that result in personal injury. The major destructive effect of sulfuric acid on skin tissue is removal of water with accompanying release of heat. Sulfuric acid decomposes carbohydrates by removal of water. In contact with sugar, for example, concentrated sulfuric acid reacts to leave a charred mass. The reaction is

$$C_{12}H_{22}O_{11} \xrightarrow{H_2SO_4} 11H_2O\,(H_2SO_4) + 12C + \text{heat} \qquad (21.6.1)$$

Some dehydration reactions of sulfuric acid can be very vigorous. For example, the reaction with perchloric acid produces unstable Cl_2O_7, and a violent explosion can result. Concentrated sulfuric acid produces dangerous or toxic products with a number of other substances, such as toxic carbon monoxide (CO) from reaction with oxalic acid, $H_2C_2O_4$; toxic bromine and sulfur dioxide (Br_2, SO_2) from reaction with sodium bromide, NaBr; and toxic, unstable chlorine dioxide (ClO_2) from reaction with sodium chlorate, $NaClO_3$.

Contact with sulfuric acid causes severe tissue destruction resulting in a severe burn that may be difficult to heal. Inhalation of sulfuric acid fumes or mists damages tissues in the upper respiratory tract and eyes. Long-term exposure to sulfuric acid fumes or mists has caused erosion of teeth.

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21.7 TOXIC SUBSTANCES

Toxicity is of the utmost concern in dealing with hazardous substances. This includes both long-term chronic effects from continual or periodic exposures to low levels of toxicants and acute effects from a single large exposure. Toxic substances are covered in greater detail in Chapter 23.

Toxicity Characteristic Leaching Procedure

For regulatory and remediation purposes, a standard test is needed to measure the likelihood of toxic substances getting into the environment and causing harm to organisms. The U.S. Environmental Protection Agency specifies a test called the **Toxicity Characteristic Leaching Procedure** (**TCLP**) designed to determine the toxicity hazard of wastes.[6] The test was designed to estimate the availability to organisms of both inorganic and organic species in hazardous materials present as liquids, solids, or multiple phase mixtures and does not test for the direct toxic effects of wastes. Basically, the procedure consists of leaching a material with a solvent designed to mimic leachate generated in a municipal waste-disposal site, followed by chemical analysis of the leachate. The procedure is discussed in more detail in Chapter 26.

21.8 PHYSICAL FORMS AND SEGREGATION OF WASTES

Three major categories of wastes based upon their physical forms are **organic materials**, **aqueous wastes**, and **sludges**. These forms largely determine the course of action taken in treating and disposing of the wastes. The **level of segregation**, a concept illustrated in Figure 21.2, is very important in treating, storing, and disposing of different kinds of wastes. It is relatively easy to deal with wastes that are not mixed with other kinds of wastes, that is, those that are highly segregated. For example, spent hydrocarbon solvents can be used as fuel in boilers. However, if these solvents are mixed with spent organochlorine solvents, the production of contaminant hydrogen chloride during combustion may prevent fuel use and require disposal in special hazardous-waste incinerators. Further mixing with inorganic sludges adds mineral matter and water. These impurities complicate the treatment processes required by producing mineral ash in incineration or lowering the heating value of the material incinerated because of the presence of water. Among the most difficult types of wastes to handle and treat are those with the least segregation, of which a "worst case scenario" would be "dilute sludge consisting of mixed organic and inorganic wastes," as shown in Figure 21.2.

Concentration of wastes is an important factor in their management. A waste that has been concentrated or, preferably, never diluted is generally much easier and more economical to handle than one that is dispersed in a large quantity of water or soil. Dealing with hazardous wastes is greatly facilitated when the original quantities of wastes are minimized and the wastes remain separated and concentrated as much as possible.

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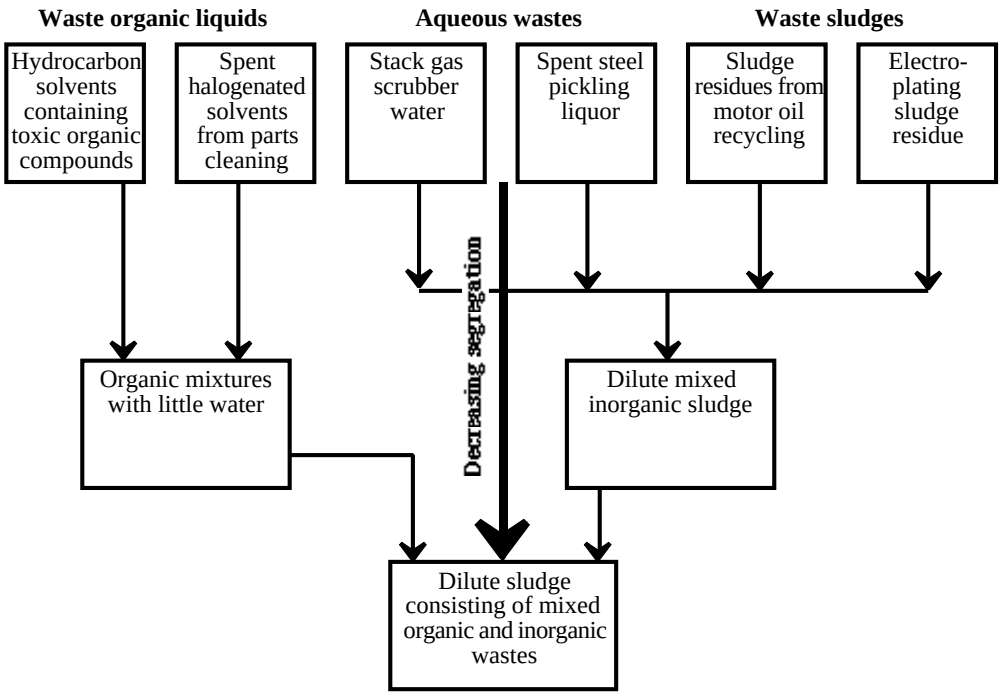


Figure 21.2 Illustration of waste segregation.

21.9 ENVIRONMENTAL CHEMISTRY OF HAZARDOUS WASTES

The properties of hazardous materials, their production, and what makes a hazardous substance a hazardous waste were discussed in preceding parts of this chapter. Hazardous materials normally cause problems when they enter the environment and have detrimental effects on organisms or other parts of the environment. Therefore, the present chapter deals with the environmental chemistry of hazardous materials. In discussing the environmental chemistry of hazardous materials, it is convenient to consider the following five aspects based upon the definition of environmental chemistry:

• Origins • Transport • Reactions • Effects • Fates

It is also useful to consider the five environmental spheres as defined and discussed in other chapters of this book:

• Anthrosphere • Geosphere • Hydrosphere • Atmosphere • Biosphere

Hazardous materials almost always originate in the anthrosphere, are often discarded into the geosphere, and are frequently transported through the hydrosphere or the atmosphere. The greatest concern for their effects is usually on the biosphere, particularly human beings. Figure 21.3 summarizes these relationships.

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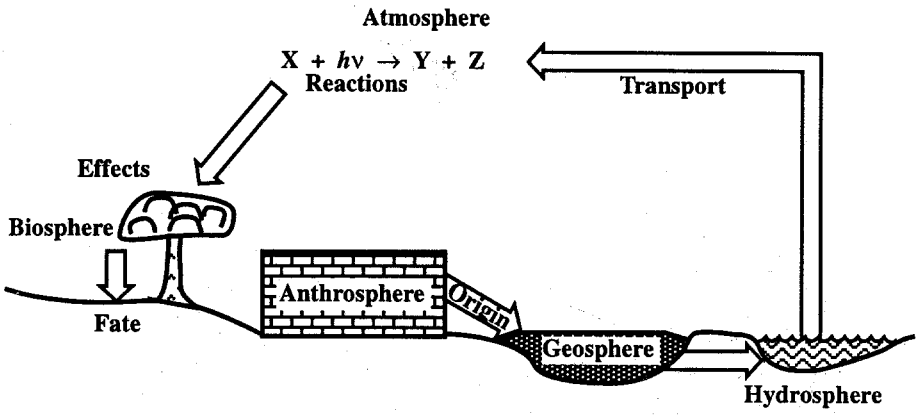


Figure 21.3 Scheme of interactions of hazardous wastes in the environment.

There are several ways in which hazardous wastes get into the environment. Although now much more controlled by pollution prevention laws, hazardous substances have been deliberately added to the environment by humans. Wastewater containing a variety of toxic substances has been discharged in large quantities into waterways. Hazardous gases and particulate matter have been discharged into the atmosphere through stacks from power plants, incinerators, and a variety of industrial operations. Hazardous wastes have been deliberately spread on soil or placed in landfills in the geosphere. Evaporation and wind erosion may move hazardous materials from wastes dumps into the atmosphere, or they may be leached from waste dumps into groundwater or surface waters. Underground storage tanks or pipelines have leaked a variety of materials into soil. Accidents, fires, and explosions may distribute dangerous materials into the environment. Another source of such materials consists of improperly operated waste treatment or storage facilities.

21.10 PHYSICAL AND CHEMICAL PROPERTIES OF HAZARDOUS WASTES

Having considered the generation of hazardous wastes from the anthrosphere, the next thing to consider is their properties, which determine movement and other kinds of behaviors. These properties can be generally divided into physical and chemical properties.

The behavior of waste substances in the atmosphere is largely determined by their volatilities. In addition, their solubilities in water determine the degree to which they are likely to be removed with precipitation. Water solubility is the most important physical property in the hydrosphere. The movement of substances through the action of water in the geosphere is largely determined by the degree of sorption to soil, mineral strata, and sediments.

Volatility is a function of the vapor pressure of a compound. Vapor pressures at a particular temperature can vary over many orders of magnitude. Of common organic liquids, diethyl ether has one of the highest vapor pressures, whereas those of polychlorinated biphenyls (PCBs) are very low. When a volatile liquid is present in soil or in water, its water solubility also determines how well it evaporates. For

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example, although methanol boils at a lower temperature than benzene, the much lower solubility of benzene in water means that it has the greater tendency to go from the hydrosphere or geosphere into the atmosphere.

The environmental movement, effects, and fates of hazardous-waste compounds are strongly related to their chemical properties. For example, a toxic heavy metal cationic species, such as Pb^{2+} ion, may be strongly held by negatively charged soil solids. If the lead is chelated by the chelating EDTA anion, represented Y^{4-}, it becomes much more mobile as PbY^{2-}, an anionic form. Oxidation state can be very important in the movement of hazardous substances. The reduced states of iron and manganese, Fe^{2+} and Mn^{2+}, respectively, are water soluble and relatively mobile in the hydrosphere and geosphere. However, in their common oxidized states, Fe(III) and Mn(IV), these elements are present as insoluble $Fe_2O_3 \cdot xH_2O$ and MnO_2, which have virtually no tendency to move. Furthermore, these iron and manganese oxides will sequester heavy metal ions, such as Pb^{2+} and Cd^{2+}, preventing their movement in the soluble form.

The major properties of hazardous substances and their surroundings that determine the environmental transport of such substances are the following:

- Physical properties of the substances, including vapor pressure and solubility.
- Physical properties of the surrounding matrix.
- Physical conditions to which wastes are subjected. Higher temperatures and erosive wind conditions enable volatile substances to move more readily.
- Chemical and biochemical properties of wastes. Substances that are less chemically reactive and less biodegradable will tend to move farther before breaking down.

21.11 TRANSPORT, EFFECTS, AND FATES OF HAZARDOUS WASTES

The transport of hazardous wastes is largely a function of their physical properties, the physical properties of their surrounding matrix, the physical conditions to which they are subjected, and chemical factors. Highly volatile wastes are obviously more likely to be transported through the atmosphere, and more soluble ones to be carried by water. Wastes will move farther faster in porous, sandy formations than in denser soils. Volatile wastes are more mobile under hot, windy conditions, and soluble ones during periods of heavy rainfall. Wastes that are more chemically and biochemically reactive will not move so far as less reactive wastes before breaking down.

Physical Properties of Wastes

The major physical properties of wastes that determine their amenability to transport are volatility, solubility, and the degree to which they are sorbed to solids, including soil and sediments.

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The distribution of hazardous-waste compounds between the atmosphere and the geosphere or hydrosphere is largely a function of compound volatility. Usually, in the hydrosphere, and often in soil, hazardous-waste compounds are dissolved in water; therefore, the tendency of water to hold the compound is a factor in its mobility. For example, although ethyl alcohol has a higher vapor pressure and lower boiling temperature (77.8˚C) than toluene (110.6 ˚C), vapor of the latter compound is more readily evolved from soil because of its limited solubility in water compared with ethanol, which is totally miscible with water.

Chemical Factors

As an illustration of chemical factors involved in transport of wastes, consider cationic inorganic species consisting of common metal ions. These inorganic species can be divided into three groups based upon their retention by clay minerals. Elements that tend to be highly retained by clay include cadmium, mercury, lead, and zinc. Potassium, magnesium, iron, silicon, and NH_4^+ ions are moderately retained by clay, whereas sodium, chloride, calcium, manganese, and boron ions are poorly retained. The retention of the last three elements is probably biased in that they are leached from clay, so that negative retention (elution) is often observed. It should be noted, however, that the retention of iron and manganese is a strong function of oxidation state in that the reduced forms of Mn and Fe are relatively poorly retained, whereas the oxidized forms of $Fe_2O_3 \cdot xH_2O$ and MnO_2 are very insoluble and stay on soil as solids.

Effects of Hazardous Wastes

The effects of hazardous wastes in the environment can be divided among effects on organisms, effects on materials, and effects on the environment. These are addressed briefly here and in greater detail in later sections.

The ultimate concern with wastes has to do with their toxic effects on animals, plants, and microbes. Virtually all hazardous-waste substances are poisonous to a degree, some extremely so. The toxicity of a waste is a function of many factors, including the chemical nature of the waste, the matrix in which it is contained, circumstances of exposure, the species exposed, manner of exposure, degree of exposure, and time of exposure. The toxicities of hazardous wastes are discussed in more detail in Chapter 23.

As defined in Section 21.6, many hazardous wastes are *corrosive* to materials, usually because of extremes of pH or because of dissolved salt content. Oxidant wastes can cause combustible substances to burn uncontrollably. Highly reactive wastes can explode, causing damage to materials and structures. Contamination by wastes, such as by toxic pesticides in grain, can result in substances' becoming unfit for use.

In addition to their toxic effects in the biosphere, hazardous wastes can damage air, water, and soil. Wastes that get into air can cause deterioration of air quality, either directly or by the formation of secondary pollutants. hazardous-waste compounds dissolved in, suspended in, or floating as surface films on the surface of water can render it unfit for use and for sustenance of aquatic organisms.

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Soil exposed to hazardous wastes can be severely damaged by alteration of its physical and chemical properties and ability to support plants. For example, soil exposed to concentrated brines from petroleum production may become unable to support plant growth so that the soil becomes extremely susceptible to erosion.

Fates of Hazardous Wastes

The fates of hazardous-waste substances are addressed in more detail in subsequent sections. As with all environmental pollutants, such substances eventually reach a state of physical and chemical stability, although that may take many centuries to occur. In some cases, the fate of a hazardous-waste material is a simple function of its physical properties and surroundings.

The fate of a hazardous-waste substance in water is a function of the substance's solubility, density, biodegradability, and chemical reactivity. Dense, water-immiscible liquids may simply sink to the bottoms of bodies of water or aquifers and accumulate there as "blobs" of liquid. This has happened, for example, with hundreds of tons of PCB wastes that have accumulated in sediments in the Hudson River in New York State. Biodegradable substances are broken down by bacteria, a process for which the availability of oxygen is an important variable. Substances that readily undergo bioaccumulation are taken up by organisms, exchangeable cationic materials become bound to sediments, and organophilic materials may be sorbed by organic matter in sediments.

The fates of hazardous-waste substances in the atmosphere are often determined by photochemical reactions. Ultimately, such substances may be converted to nonvolatile, insoluble matter and precipitate from the atmosphere onto soil or plants.

21.12 HAZARDOUS WASTES AND THE ANTHROSPHERE

As the part of the environment where humans process substances, the anthrosphere is the source of most hazardous wastes. These materials may come from manufacturing, transportation activities, agriculture, and any one of a number of activities in the anthrosphere. Hazardous wastes may be in any physical form and may include liquids, such as spent halogenated solvents used in degreasing parts; semisolid sludges, such as those generated from the gravitation separation of oil-water-solids mixtures in petroleum refining; and solids, such as baghouse dusts from the production of pesticides.

Releases of hazardous wastes from the anthrosphere commonly occur through incidents such as spills of liquids, accidental discharge of gases or vapors, fires, and explosions.[7] Resource Conservation and Recovery Act (RCRA) regulations designed to minimize such accidental releases from the anthrosphere and to deal with them when they occur are contained in 40 CFR 265.31 (Title 40 of the Code of Federal Regulations, Part 265.31). Under these regulations, hazardous-waste generators are required to have specified equipment, trained personnel, and procedures that protect human health in the event of a release, and that facilitate remediation if a release occurs. An effective means of communication for summoning help and giving emergency instruction must be available. Also required are firefighting capabilities including fire extinguishers and adequate water. To deal with spills, a facility is

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required to have on hand absorbents, such as granular vermiculite clay, or absorbents in the form of pillows or pads. Neutralizing agents for corrosive substances that may be used should be available as well.

As noted above, hazardous wastes originate in the anthrosphere. However, to a large extent, they move, have effects, and end up in the anthrosphere as well. Large quantities of hazardous substances are moved by truck, rail, ship, and pipeline. Spills and releases from such movement, ranging from minor leaks from small containers to catastrophic releases of petroleum from wrecked tanker ships, are a common occurrence. Much effort in the area of environmental protection can be profitably devoted to minimizing and increasing the safety of the transport of hazardous substances through the anthrosphere.

In the United States, the transportation of hazardous substances is regulated through the U.S. Department of Transportation (DOT). One of the ways in which this is done is through the **manifest** system of documentation designed to accomplish the following goals:

- Act as a tracking device to establish responsibility for the generation, movement, treatment, and disposal of the waste.
- By requiring the manifest to accompany the waste, such as during truck transport, it provides information regarding appropriate actions to take during emergencies such as collisions, spills, fires, or explosions.
- Act as the basic documentation for recordkeeping and reporting.

Many of the adverse effects of hazardous substances occur in the anthrosphere. One of the main examples of such effects occurs as corrosion of materials that are strongly acidic or basic or that otherwise attack materials. Fire and explosion of hazardous materials can cause severe damage to anthrospheric infrastructure.

The fate of hazardous materials is often in the anthrosphere. One of the main examples of a material dispersed in the anthrosphere consists of lead-based anti-corrosive paints that are spread on steel structural members.

21.13 HAZARDOUS WASTES IN THE GEOSPHERE

The sources, transport, interactions, and fates of contaminant hazardous wastes in the geosphere involve a complex scheme, some aspects of which are illustrated in Figure 21.4. As illustrated in the figure, there are numerous vectors by which hazardous wastes can get into groundwater. Leachate from a landfill can move as a waste plume carried along by groundwater, in severe cases draining into a stream or into an aquifer where it may contaminate well water. Sewers and pipelines may leak hazardous substances into the geosphere. Such substances seep from waste lagoons into geological strata, eventually contaminating groundwater. Wastes leaching from sites where they have been spread on land for disposal or as a means of treatment can contaminate the geosphere and groundwater. In some cases, wastes are pumped into deep wells as a means of disposal.

The movement of hazardous-waste constituents in the geosphere is largely by the action of flowing water in a waste plume, as shown in Figure 21.4. The speed and degree of waste flow depend upon numerous factors. Hydrologic factors such as

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water gradient and permeability of the solid formations through which the waste plume moves are important. The rate of flow is usually rather slow, typically several centimeters per day. An important aspect of the movement of wastes through the geosphere is **attenuation** by the mineral strata. This occurs because waste compounds are sorbed to solids by various mechanisms. A measure of the attenuation can be expressed by a **distribution coefficient**, K_d,

$$K_d = \frac{C_S}{C_W} \tag{9.13.1}$$

where C_S and C_W are the equilibrium concentrations of the constituent on solids and in solution, respectively. This relationship assumes relatively ideal behavior of the hazardous substance that is partitioned between water and solids (the sorbate). A more empirical expression is based on the Freundlich equation,

$$C_S = K_F C_{eq}^{1/n} \tag{9.13.2}$$

where and K_F and 1/n are empirical constants.

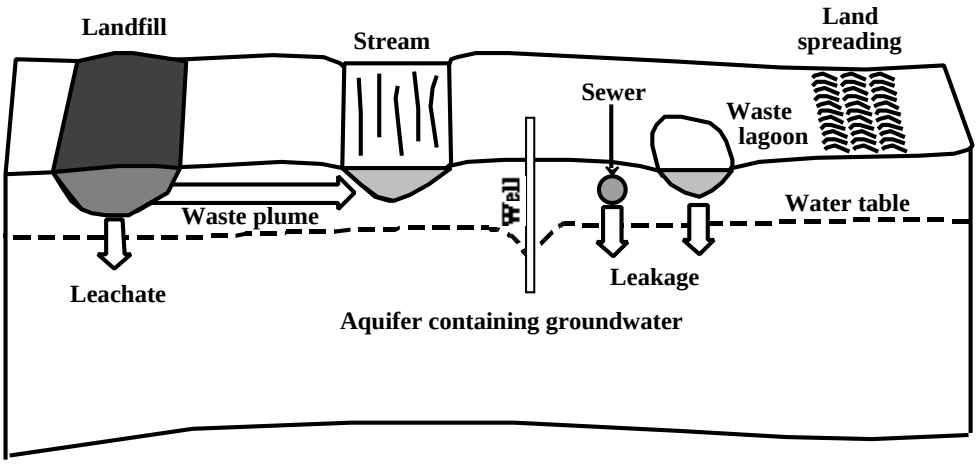


Figure 21.4 Sources and movement of hazardous wastes in the geosphere.

Several important properties of the solid determine the degree of sorption. One obvious factor is surface area. The chemical nature of the surface is also important. Among the important chemical factors are presence of sorptive clays, hydrous metal oxides, and humus (particularly important for the sorption of organic substances).

In general, sorption of hazardous-waste solutes is higher above the water table in the unsaturated zone of soil. This region tends to have a higher surface area and to favor aerobic biodegradation processes.

The chemical nature of the leachate is important in sorptive processes of hazardous substances in the geosphere. Organic solvents or detergents in leachates will solubilize organic materials, preventing their retention by solids. Acidic leachates tend to dissolve metal oxides,

$$M(OH)_2(s) + 2H^+ \rightarrow M^{2+} + 2H_2O \tag{9.13.3}$$

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thus preventing sorption of metals in insoluble forms. This is a reason that leachates from municipal landfills, which contain weak organic acids, are particularly prone to transport metals. Solubilization by acids is particularly important in the movement of heavy-metal ions.

Heavy metals are among the most dangerous hazardous-waste constituents that are transported through the geosphere. Many factors affect their movement and attenuation. The temperature, pH, and reducing nature (as expressed by the negative log of the electron activity, pE) of the solvent medium are important. The nature of the solids, especially the inorganic and organic chemical functional groups on the surface, the cation-exchange capacity, and the surface area of the solids largely determine the attenuation of heavy-metal ions. In addition to being sorbed and undergoing ion exchange with geospheric solids, heavy metals may undergo oxidation-reduction processes, precipitate as slightly soluble solids (especially sulfides), and in some cases, such as occurs with mercury, undergo microbial methylation reactions that produce mobile organometallic species.

The importance of chelating agents interacting with metals and increasing their mobilities has been illustrated by the effects of chelating ethylenediaminetetraacetic acid (EDTA) on the mobility of radioactive heavy metals, especially ^{60}Co.[8] The EDTA and other chelating agents, such as diethylenetriaminepentaacetic acid (DTPA) and nitrilotriacetic acid (NTA), were used to dissolve metals in the decontamination of radioactive facilities and were codisposed with radioactive materials at Oak Ridge National Laboratory (Tennessee) during the period 1951–1965. Unexpectedly high rates of radioactive metal mobility were observed, which was attributed to the formation of anionic species such as $^{60}CoT^-$ (where T^{3-} is the chelating NTA anion). Whereas unchelated cationic metal species are strongly retained on soil by precipitation reactions and cation exchange processes,

$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2(s) \tag{9.13.4}$$

$$2Soil\}^-H^+ + Co^{2+} \rightarrow (Soil\}^-)_2Co^{2+} + 2H^+ \tag{9.13.5}$$

anion bonding processes are very weak, so that the chelated anionic metal species are not strongly bound. Naturally occurring humic acid chelating agents may also be involved in the subsurface movement of radioactive metals. It is now generally accepted that poorly biodegradable, strong chelating agents, of which EDTA is the prime example, will facilitate transport of metal radionuclides, whereas oxalate and citrate will not do so because they form relatively weak complexes and are readily biodegraded.[9] Biodegradation of chelating agents tends to be a slow process under subsurface conditions.

Soil can be severely damaged by hazardous-waste substances. Such materials may alter the physical and chemical properties of soil and thus its ability to support plants. Some of the more catastrophic incidents in which soil has been damaged by exposure to hazardous materials have arisen from soil contamination from SO_2 emitted from copper or lead smelters, or from brines from petroleum production. Both of these contaminants stop the growth of plants and, without the binding effects of viable plant root systems, topsoil is rapidly lost by erosion.

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Unfortunate cases of the improper disposal of hazardous wastes into the geosphere have occurred throughout the world. For example, in December 1998 it was alleged that Formosa Plastics had disposed of 3000 tons of mercury-containing wastes in Cambodia, the result of byproduct sludge generated by the chloralkali electrolytic prcess for generating chlorine and sodium hydroxide. Subsequently, illegal dump sites containing mercury were found in many places in Taiwan, causing major environmental concerns.[10]

21.14 HAZARDOUS WASTES IN THE HYDROSPHERE

Hazardous-waste substances can enter the hydrosphere as leachate from waste landfills, drainage from waste ponds, seepage from sewer lines, or runoff from soil. Deliberate release into waterways also occurs, and is a particular problem in countries with lax environmental enforcement. There are, therefore, numerous ways by which hazardous materials may enter the hydrosphere.

For the most part, the hydrosphere is a dynamic, moving system, so that it provides perhaps the most important variety of pathways for moving hazardous-waste species in the environment. Once in the hydrosphere, hazardous-waste species can undergo a number of processes by which they are degraded, retained, and transformed. These include the common chemical processes of precipitation-dissolution, acid-base reactions, hydrolysis, and oxidation-reduction reactions. Also included is a wide variety of biochemical processes which, in most cases, reduce hazards, but in some cases, such as the biomethylation of mercury, greatly increase the risks posed by hazardous wastes.

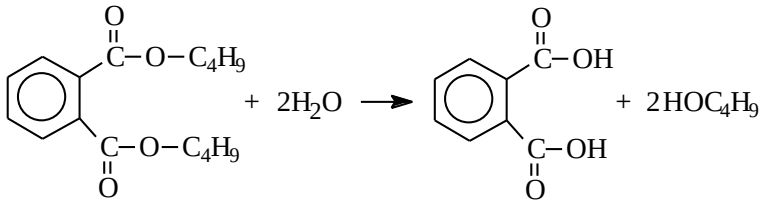
The unique properties of water have a strong influence on the environmental chemistry of hazardous wastes in the hydrosphere. Aquatic systems are subject to constant change. Water moves with groundwater flow, stream flow, and convection currents. Bodies of water become stratified so that low-oxygen reducing conditions may prevail in the bottom regions of a body of water, and there is a constant interaction of the hydrosphere with the other environmental spheres. There is a continuing exchange of materials between water and the other environmental spheres. Organisms in water may have a strong influence on even poorly biodegradable hazardous-waste species through bioaccumulation mechanisms.

Figure 21.5 shows some of the pertinent aspects of hazardous-waste materials in bodies of water, with emphasis upon the strong role played by sediments. An interesting kind of hazardous-waste material that may accumulate in sediments consists of dense, water-immiscible liquids that can sink to the bottom of bodies of water or aquifers and remain there as “blobs” of liquid. Hundreds of tons of PCB wastes have accumulated in sediments in the Hudson River in New York State and are the subject of a heated debate regarding how to remediate the problem.

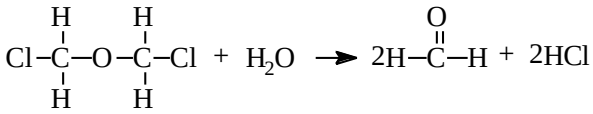
Hazardous-waste species undergo a number of physical, chemical, and biochemical processes in the hydrosphere that strongly influence their effects and fates. The major ones are listed below:

- **Hydrolysis reactions** are those in which a molecule is cleaved with addition of a molecule of H_2O. An example of a hydrolysis reaction is the hydrolysis of dibutyl phthalate, Hazardous Waste Number U069:

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Another example is the hydrolysis of bis(chloromethyl)ether to produce HCl and formaldehyde:



Compounds that hydrolyze are normally those, such as esters and acid anhydrides, originally formed by joining two other molecules with the loss of H_2O.

- **Precipitation reactions**, such as the formation of insoluble lead sulfide from soluble lead(II) ion in the anaerobic regions of a body of water:

$$Pb^{2+} + HS^- \rightarrow PbS(s) + H^+$$

An important part of the precipitation process is normally **aggregation** of the colloidal particles first formed to produce a cohesive mass. Precipitates are often relatively complicated species, such as the basic salt of lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$. Heavy metals, a common ingredient of hazardous-waste species precipitated in the hydrosphere, tend to form hydroxides, carbonates, and sulfates with the OH^-, HCO_3^-, and SO_4^{2-} ions

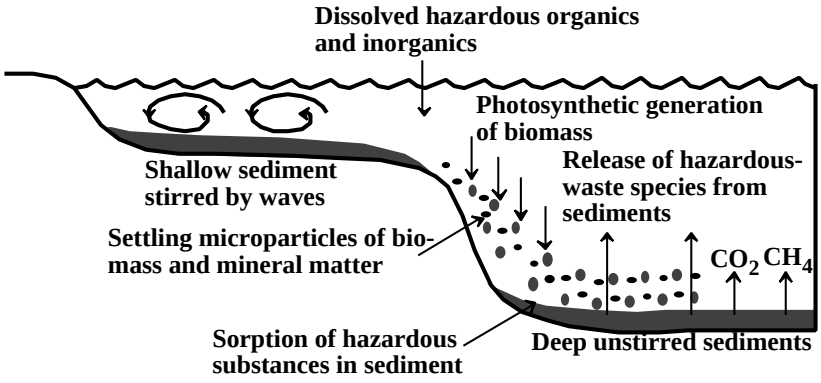


Figure 21.5 Aspects of hazardous wastes in surface water in the hydrosphere. The deep unstirred sediments are anaerobic and the site of hydrolysis reactions and reductive processes that may act on hazardous-waste constituents sorbed to the sediment.

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that commonly are present in water, and sulfides are likely to be formed in bottom regions of bodies of water where sulfide is generated by anaerobic bacteria. Heavy metals are often coprecipitated as a minor constituent of some other compound, or are sorbed by the surface of another solid.

- **Oxidation-reduction reactions** commonly occur with hazardous-waste materials in the hydrosphere, generally mediated by microorganisms. An example of such a process is the oxidation of ammonia to toxic nitrite ion mediated by *Nitrosomonas* bacteria:

$$NH_3 + {}^3/_2O_2 \rightarrow H^+ + NO_2^-(s) + H_2O$$

- **Biochemical processes**, which often involve hydrolysis and oxidation-reduction reactions. Organic acids and chelating agents, such as citrate, produced by bacterial action may solubilize heavy metal ions. Bacteria also produce methylated forms of metals, particularly mercury and arsenic.

- **Photolysis reactions** and miscellaneous chemical phenomena. Photolysis of hazardous-waste compounds in the hydrosphere commonly occurs on surface films exposed to sunlight on the top of water.

Hazardous-waste compounds have a number of effects on the hydrosphere. Perhaps the most serious of these is the contamination of groundwater, which in some cases can be almost irreversible. Waste compounds accumulate in sediments, such as river or estuary sediments. Hazardous-waste compounds dissolved in, suspended in, or floating as surface films on the surface of water can render it unfit for use and for sustenance of aquatic organisms.

Many factors determine the fate of a hazardous-waste substance in water. Among these are the substance's solubility, density, biodegradability, and chemical reactivity. As discussed above and in Section 21.16, biodegradation largely determines the fates of hazardous-waste substances in the hydrosphere. In addition to biodegradation, some substances are concentrated in organisms by bioaccumulation processes and may become deposited in sediments as a result. Organophilic materials may be sorbed by organic matter in sediments. Cation-exchanging sediments have the ability to bind cationic species, including cationic metal ions and organics that form cations.

21.15 HAZARDOUS WASTES IN THE ATMOSPHERE

Hazardous-waste chemicals can enter the atmosphere by evaporation from hazardous-waste sites, by wind erosion, or by direct release. Hazardous-waste chemicals usually are not evolved in large enough quantities to produce secondary air pollutants. (Secondary air pollutants are formed by chemical processes in the atmosphere. Examples are sulfuric acid formed from emissions of sulfur oxides and oxidizing photochemical smog formed under sunny conditions from nitrogen oxides and hydrocarbons.) Therefore, species from hazardous-waste sources are usually of most concern in the atmosphere as primary pollutants emitted in localized areas at a

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hazardous-waste site. Plausible examples of primary air pollutant hazardous-waste chemicals include corrosive acid gases, particularly HCl; toxic organic vapors, such as vinyl chloride (U043); and toxic inorganic gases, such as HCN potentially released by the accidental mixing of waste cyanides:

$$H_2SO_4 + 2NaCN \rightarrow Na_2SO_4 + 2HCN(g) \quad (21.15.1)$$

Primary air pollutants such as these are almost always of concern only adjacent to the site or to workers involved in site remediation. One such substance that has been responsible for fatal poisonings at hazardous-waste sites, usually tanks that are undergoing cleanup or demolition, is highly toxic hydrogen sulfide gas, H_2S.

An important characteristic of a hazardous-waste material that enters the atmosphere is its **pollution potential**. This refers to the degree of environmental threat posed by the substance acting as a primary pollutant, or to its potential to cause harm from secondary pollutants.

Another characteristic of a hazardous-waste material that determines its threat to the atmosphere is its **residence time**, which can be expressed by an estimated atmospheric half-life, $\tau_{1/2}$. Among the factors that go into estimating atmospheric half-lives are water solubilities, rainfall levels, and atmospheric mixing rates.

Hazardous-waste compounds in the atmosphere that have significant water solubilities are commonly removed from the atmosphere by **dissolution** in water. The water may be in the form of very small cloud or fog particles or it may be present as rain droplets.

Some hazardous-waste species in the atmosphere are removed by **adsorption onto aerosol particles**. Typically, the adsorption process is rapid so that the lifetime of the species is that of the aerosol particles (typically a few days). Adsorption onto solid particles is the most common removal mechanism for highly nonvolatile constituents such as benzo[a]pyrene.

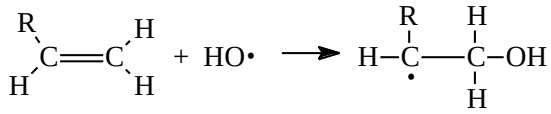
Dry deposition is the name given to the process by which hazardous-waste species are removed from the atmosphere by impingement onto soil, water, or plants on the earth's surface. These rates are dependent upon the type of substance, the nature of the surface that they contact, and weather conditions.

A significant number of hazardous-waste substances leave the atmosphere much more rapidly than predicted by dissolution, adsorption onto particles, and dry deposition, meaning that chemical processes must be involved. The most important of these are photochemical reactions, commonly involving hydroxyl radical, $HO^{\bullet}$. Other reactive atmospheric species that may act to remove hazardous-waste compounds are ozone (O_3), atomic oxygen (O), peroxyl radicals ($HOO^{\bullet}$), alkyl-peroxyl radicals ($ROO^{\bullet}$), and NO_3. Although its concentration in the troposphere is relatively low, $HO^{\bullet}$ is so reactive that it tends to predominate in the chemical processes that remove hazardous-waste species from air. Hydroxyl radical undergoes *abstraction reactions* that remove H atoms from organic compounds,

$$R\text{-}H + HO^{\bullet} \rightarrow R^{\bullet} + H_2O \quad (9.15.2)$$

and may react with those containing unsaturated bonds by addition as illustrated by the following reaction:

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(9.15.3)

The free radical products are very reactive. They react further to form oxygenated species, such as aldehydes, ketones, and dehalogenated organics, eventually leading to the formation of particles or water-soluble materials that are readily scavenged from the atmosphere.

Direct photodissociation of hazardous-waste compounds in the atmosphere may occur by the action of the shorter wavelength light that reaches to the troposphere and is absorbed by a molecule with a light-absorbing group called a **chromophore**:

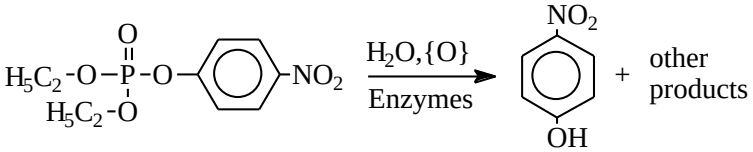
$$R–X + h\nu \rightarrow R^{\bullet} + X^{\bullet} \qquad (9.15.4)$$

Among the factors involved in assessing the effectiveness of direct absorption of light to remove species from the atmosphere are light intensity, quantum yields (chemical reactions per quantum absorbed), and atmospheric mixing. The requirement of a suitable chromophore limits direct photolysis as a removal mechanism for most compounds other than conjugated alkenes, carbonyl compounds, some halides, and some nitrogen compounds, particularly nitro compounds, all of which commonly occur in hazardous wastes.

21.16 HAZARDOUS WASTES IN THE BIOSPHERE

Microorganisms, bacteria, fungi, and, to a certain extent, protozoa may act metabolically on hazardous-waste substances in the environment. Most of these substances are *anthropogenic* (made by human activities), and most are classified as *xenobiotic* molecules that are foreign to living systems. Although by their nature xenobiotic compounds are degradation resistant, almost all classes of them—nonhalogenated alkanes, halogenated alkanes (trichloroethane, dichloromethane), nonhalogenated aryl compounds (benzene, naphthalene, benzo[a]pyrene), halogenated aryl compounds (hexachlorobenzene, pentachlorophenol), phenols (phenol, cresols), polychlorinated biphenyls, phthalate esters, and pesticides (chlordane, parathion)—can be at least partially degraded by various microorganisms.

Bioaccumulation occurs in which wastes are concentrated in the tissue of organisms. It is an important mechanism by which wastes enter food chains. **Biodegradation** occurs when wastes are converted by biological processes to generally simpler molecules; the complete conversion to simple inorganic species, such as CO_2, NH_3, SO_4^{2-}, and $H_2PO_4^-/HPO_4^-$, is called **mineralization.** The production of a less toxic product by biochemical processes is called **detoxification**. An example is the bioconversion of highly toxic organophosphate paraoxon to *p*-nitrophenol, which is only about l/200 as toxic:



(21.16.1)

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Microbial Metabolism in Waste Degradation

The following terms and concepts apply to the metabolic processes by which microorganisms biodegrade hazardous-waste substances:

- **Biotransformation** is the enzymatic alteration of a substance by microorganisms.
- **Metabolism** is the biochemical process by which biotransformation is carried out.
- **Catabolism** is an enzymatic process by which more-complex molecules are broken down into less complex ones.
- **Anabolism** is an enzymatic process by which simple molecules are assembled into more-complex biomolecules.

Two major divisions of biochemical metabolism that operate on hazardous-waste species are **aerobic processes** that use molecular O_2 as an oxygen source and **anaerobic processes**, which make use of another oxidant. For example, when sulfate ion acts as an oxidant (electron receptor) the transformation $SO_4^{2-} \rightarrow H_2S$ occurs. (This has the benefit of providing sulfide, which precipitates insoluble metal sulfides in the presence of hazardous waste heavy metals.) Because molecular oxygen does not penetrate to such depths, anaerobic processes predominate in the deep sediments, as shown in Figure 21.5.

For the most part, anthropogenic compounds resist biodegradation much more strongly than do naturally occurring compounds. Given the nature of xenobiotic substances, there are very few enzyme systems in microorganisms that act directly on these substances, especially in making an intial attack on the molecule. Therefore, most xenobiotic compounds are acted upon by a process called **cometabolism**, which occurs concurrently with normal metabolic processes. An interesting example of cometabolism is provided by the white rot fungus, *Phanerochaete chrysosporium*, which has been promoted for the treatment of hazardous organochlorides such as PCBs, DDT, and chlorodioxins. This fungus uses dead wood as a carbon source and has an enzyme system that breaks down wood lignin, a degradation-resistant biopolymer that binds the cellulose in wood. Under appropriate conditions, this enzyme system attacks organochloride compounds and enables their mineralization.

The susceptibility of a xenobiotic hazardous-waste compound to biodegradation depends upon its physical and chemical characteristics. Important physical characteristics include water solubility, hydrophobicity (aversion to water), volatility, and lipophilicity (affinity for lipids). In organic compounds, certain structural groups—branched carbon chains, ether linkages, meta-substituted benzene rings, chlorine, amines, methoxy groups, sulfonates, and nitro groups—impart particular resistance to biodegradation.

Microorganisms vary in their ability to degrade hazardous-waste compounds; virtually never does a single microorganism have the ability to completely mineralize a waste compound. Abundant aerobic bacteria of the ***Pseudomonas***

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family are particularly adept at degrading synthetic compounds such as biphenyl, naphthalene, DDT, and many other compounds. ***Actinomycetes***, microorganisms that are morphologically similar to both bacteria and fungi, degrade a variety of organic compounds including degradation-resistant alkanes and lignocellulose, as well as pyridines, phenols, nonchlorinated aryls, and chlorinated aryls.

Because of their requirement for oxygen-free (anoxic) conditions, anaerobic bacteria are fastidious and difficult to study. However, they can play an important role in degrading biomass, particularly through hydrolytic processes in which molecules are cleaved with addition of H_2O. Anaerobic bacteria reduce oxygenated organic functional groups. As examples, they convert nitro compounds to amines, degrade nitrosamines, promote reductive dechlorination, reduce epoxide groups to alkenes, and break down aryl structures. Partial dechlorination of PCBs by bacteria growing anaerobically in PCB-contaminated river sediments such as those in New York's Hudson River has been reported.[11] PCB waste remediation schemes have been proposed that make use of anaerobic dechlorination of the more highly chlorinated PCBs and aerobic degradation of the less highly chlorinated products.[12]

Fungi are particularly noted for their ability to attack long-chain and complex hydrocarbons, and are more successful than bacteria in the initial attack on PCB compounds. The potential of the white rot fungus, *Phanerochaete chrysosporium*, to degrade biodegradation-resistant compounds, especially organochloride species, was previously noted.

Phototrophic microorganisms, algae, photosynthetic bacteria, and cyanobacteria that perform photosynthesis have lipid bodies that accumulate lipophilic compounds. There is some evidence to suggest that these organisms can induce photochemical degradation of the stored compounds.

Biologically, the greatest concern with wastes has to do with their toxic effects on animals, plants, and microbes. Virtually all hazardous-waste substances are poisonous to a degree, some extremely so. Toxicities vary markedly with the physical and chemical nature of the waste, the matrix in which it is contained, the type and condition of the species exposed, and the manner, degree, and time of exposure.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

A **hazardous substance** is a material that [1]_____

and a hazardous waste is [2]_____

_____.
The [3]_____ affair of the 1970s and 1980s brought hazardous-wastes to public attention as a major political issue in the U.S. In the U.S., RCRA stands for

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the [4]_____. Two means of classifying wastes are by [5]_____ and as [6]_____ wastes. Four recognized characteristics of hazardous wastes are [7]_____ _____. Four major classes of listed wastes are [8]_____ _____ _____. Among the kinds of hazardous wastes produced by water pollution control are [9]___ _____ and among those produced by air pollution control measures are [10]_____. Liquids that pose fire hazards form flammable [11]_____. The tendency of a liquid to burn is determined by measuring its [12]_____. In considering the ignition of vapors, two important concepts are those of [13]_____ _____. [14]_____ occur with the rapid burning of solids, such as finely divided coal or metal powders. A type of substance that may react dangerously with combustible substances consists of [15]_____ _____, one of which that releases toxic NO_2 as a product is [16]_____. Substances that catch fire spontaneously in air without an ignition source are [17]____ _____ substances. Mixtures of oxidizers and oxidizable chemicals that catch fire spontaneously are called [18]_____, of which a mixture of phenol and [19]_____ is an example. The most obvious toxic product of combustion is [20]_____. Reactive substances are those that [21]_____ _____ under certain conditions. Nitroglycerin is a self-reactive that contains [22]_____ _____ in the same compound. High reactivity in organic compounds can result from structural features such as [23]_____ _____ _____. Corrosive substances are those that affect metals by [24]_____ _____ or more broadly cause [25]_____. Four general classes of corrosive substances are [26]_____ _____. For regulatory and remediation purposes toxic substances are determined by a test called [27]_____. Three major categories of wastes based upon their physical forms are [28]_____ _____. It is much easier to deal with wastes that have been maintained at a high level of [29]_____. In discussing the environmental chemistry of hazardous materials, it is convenient to consider the five aspects of [30]_____ based upon the definition of environmental chemistry within the five physical locations of [31]_____ _____. Hazardous materials almost always originate in the [32]_____, are often discarded into the [33]_____, and are frequently transported through [34]_____. The behavior of waste substances in the atmosphere is determined for the most part by their [35]_____ whereas [36]_____ is the most important

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physical property in the hydrosphere. The major properties of hazardous substances and their surroundings that determine the environmental transport of such substances are [37]_____

_____.
The major physical properties of wastes that determine their amenability to transport are [38]_____
_____. The effects of hazardous wastes in the environment may be divided among the three categories of [39]_____
_____. The fate of a hazardous-waste substance in water is a function of the substance's [40]_____
_____. The fates of hazardous-waste substances in the atmosphere are often determined by [41]_____ reactions. Regulation of the transport of hazardous wastes by truck or other means is through a [42]_____ system of documentation. An important aspect of the movement of wastes through the geosphere is [43]_____ by the mineral strata, a measure of which can be expressed by a [44]_____. Radioactive ^{60}Co disposed in the geosphere has been found to be more mobile than expected in some cases because of codisposal with [45]_____. Some of the important processes that hazardous wastes undergo in the hydrosphere are [46]_____
_____.
Hazardous-waste compounds in the atmosphere that have significant water solubilities are commonly removed from the atmosphere by [47]_____
_____ whereas removal by impingement onto soil, water, or plants on the earth's surface is called [48]_____. The most important reactive species involved in removing hazardous-waste compounds from the atmosphere is [49]_____. Direct photodissociation of hazardous-waste compounds in the atmosphere may occur if the molecule possesses a [50]_____
_____. Most hazardous-waste compounds encountered by organisms in the biosphere are classified as [51]_____ molecules that are foreign to living systems. [52]_____ occurs when wastes are concentrated in the tissue of organisms. [53]_____ occurs when wastes are converted by biological processes to generally simpler molecules and mineralization is [54]____
_____.
Theproduction of a less toxic product by biochemical processes is called [55]_____
_____. Two major divisions of biochemical metabolism that operate on hazardous-waste species based upon oxygen requirement are [56]_____
_____. Most xenobiotic compounds are acted upon by organisms through a process called [57]_____.

Answers to Chapter Summary

1. may pose a danger to living organisms, materials, structures, or the environment by explosion or fire hazards, corrosion, toxicity to organisms, or other detrimental effects

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2. a hazardous substance that has been discarded, abandoned, neglected, released or designated as a waste material, or one that may interact with other substances to be hazardous
3. Love Canal
4. Resource Conservation and Recovery Act
5. characteristics
6. listed
7. ignitability, corrosivity, reactivity, and toxicity
8. F-type wastes from nonspecific sources, K-type wastes from specific sources, P-type acute hazardous wastes, and U-Type miscellaneous hazardous wastes
9. sludges and concentrated liquors
10. sludges and solids
11. vapors
12. flash point
13. flammability limit and flammability range
14. Dust explosions
15. oxidizers
16. concentrated HNO_3
17. pyrophoric
18. hypergolic mixtures
19. nitric acid
20. carbon monoxide
21. tend to undergo rapid or violent reactions
22. oxidant and reductant
23. unsaturated bonds in proximity in the carbon skeleton and functional groups containing both oxygen and nitrogen
24. dissolving them or causing corroded surfaces to form on them
25. deterioration of materials
26. (1) strong acids, (2) strong bases, (3) oxidants, and (4) dehydrating agents
27. the Toxicity Characteristic Leaching Procedure, TCLP
28. organic materials, aqueous wastes, and sludges
29. segregation
30. origins, transport, reactions, effects, and fates
31. the anthrosphere, the geosphere, the hydrosphere, the atmosphere, and the biosphere
32. anthrosphere
33. geosphere
34. the hydrosphere or the atmosphere
35. volatilities
36. water solubility
37. physical properties of the substances, physical properties of the surrounding matrix, physical conditions to which wastes are subjected, and chemical and biochemical properties of wastes
38. volatility, solubility, and the degree to which they are sorbed to solids
39. effects on organisms, effects on materials, and effects on the environment
40. solubility, density, biodegradability, and chemical reactivity
41. photochemical

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42. manifest
43. attenuation
44. distribution coefficient, K_d
45. chelating agents
46. precipitation-dissolution, acid-base reactions, hydrolysis, oxidation-reduction reactions, and biological processes
47. dissolution in water
48. dry impingement
49. hydroxyl radical, HO·
50. chromophore
51. xenobiotic
52. Bioaccumulation
53. Biodegradation
54. the complete conversion to simple inorganic species
55. detoxification
56. aerobic processes and anaerobic processes
57. cometabolism

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QUESTIONS AND PROBLEMS

1. Match the following kinds of hazardous substances on the left with a specific example of each from the right, below:

1.Explosives	(a) Oleum, sulfuric acid, caustic soda
2.Compressed gases	(b) White phosphorus
3.Radioactive materials	(c) NH_4ClO_4
4.Flammable solids	(d) Hydrogen, sulfur dioxide
5.Oxidizing materials	(e) Nitroglycerin
6.Corrosive materials	(f) Plutonium, cobalt-60

2. Of the following, the property that is **not** a member of the same group as the other properties listed is (a) substances that are liquids whose vapors are likely to ignite in the presence of ignition sources, (b) nonliquids that may catch fire from friction or contact with water and thay burn vigorously or persistently, (c) ignitable compressed gases, (d) oxidizers, (e) substances that exhibit extremes of acidity or basicity.

3. In what respects can it be said that measures taken to alleviate air and water pollution tend to aggravate hazardous-waste problems?

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4. Why is attenuation of metals likely to be very poor in acidic leachate? Why is attenuation of anionic species in soil less than that of cationic species?
5. Discuss the significance of LFL, UFL, and flammability range in determining the flammability hazards of organic liquids.
6. Concentrated HNO_3 and its reaction products pose several kinds of hazards. What are these?
7. What are substances called that catch fire spontaneously in air without an ignition source?
8. Name four or five hazardous products of combustion and specify the hazards posed by these materials.
9. What kind of property tends to be imparted to a functional group of an organic compound containing both oxygen and nitrogen?
10. Match the corrosive substance from the column on the left, below, with one of its major properties from the right column:

1. Alkali metal hydroxides	(a) Reacts with protein in tissue to form yellow xanthoproteic acid
2. Hydrogen peroxide	
3. Hydrofluoric acid, HF	(b) Dissolves glass
4. Nitric acid, HNO_3	(c) Strong bases
	(d) Oxidizer

11. Rank the following wastes in increasing order of segregation (a) mixed halogenated and hydrocarbon solvents containing little water, (b) spent steel pickling liquor, (c) dilute sludge consisting of mixed organic and inorganic wastes, (d) spent hydrocarbon solvents free of halogenated materials, (e) dilute mixed inorganic sludge.
12. Inorganic species can be divided into three major groups based upon their retention by clays. What are the elements commonly listed in these groups? What is the chemical basis for this division? How might anions (Cl^-, NO_3^-) be classified?
13. In what form would a large quantity of hazardous-waste PCB likely be found in the hydrosphere?
14. The Toxicity Characteristic Leaching Procedure was originally devised to mimic a “mismanagement scenario” in which hazardous wastes were disposed of along with biodegradable organic municipal refuse. Discuss how this procedure reflects the conditions that might arise from circumstances in which hazardous wastes and actively decaying municipal refuse were disposed of together.
15. What are three major properties of wastes that determine their amenability to transport?
16. List and discuss the significance of major sources for the origin of hazardous wastes, that is, their main modes of entry into the environment. What are the relative dangers posed by each of these? Which part of the environment would each be most likely to contaminate?

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17. What is the influence of organic solvents in leachates upon attenuation of organic hazardous waste constituents?
18. What features or characteristics should a compound possess for direct photolysis to be a significant factor in its removal from the atmosphere?
19. Describe the particular danger posed by codisposal of strong chelating agents with radionuclide wastes. What can be said about the chemical nature of the latter with regard to this danger?
20. Describe a beneficial effect that might result from the precipitation of either $Fe_2O_3 \cdot xH_2O$ or $MnO_2 \cdot xH_2O$ from hazardous wastes in water.
21. Why are secondary air pollutants from hazardous-waste sites usually of only limited concern as compared with primary air pollutants? What is the distinction between the two?
22. Match the following physical, chemical, and biochemical processes dealing with the transformations and ultimate fates of hazardous chemical species in the hydrosphere on the left with the description of the process on the right, below:

1. Precipitation reactions	(a) Molecule is cleaved with the addition of H_2O
2. Biochemical processes	(b) Generally accompanied by aggregation of colloidal particles suspended in water
3. Oxidation-reduction	
4. Hydrolysis reactions	(c) Generally mediated by microorganisms
5. Sorption	(d) By sediments and by suspended matter
	(e) Often involve hydrolysis and oxidation-reduction

23. As applied to hazardous wastes in the biosphere, distinguish among biodegradation, biotransformation, detoxification, and mineralization.
24. What is the potential role of *Phanerochaete chrysosporium* in treatment of hazardous-waste compounds? For which kinds of compounds might it be most useful?
25. Which part of the hydrosphere is most subject to long-term, largely irreversible contamination from the improper disposal of hazardous wastes in the environment?
26. Several physical and chemical characteristics are involved in determining the amenability of a hazardous waste compound to biodegradation. These include hydrophobicity, solubility, volatility, and affinity for lipids. Suggest and discuss ways in which each one of these factors might affect biodegradability.
27. List and discuss some of the important processes determining the transformations and ultimate fates of hazardous chemical species in the hydrosphere.

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Fundamentals of Environmental Chemistry
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22 INDUSTRIAL ECOLOGY FOR WASTE MINIMIZATION, UTILIZATION, AND TREATMENT

22.1 INTRODUCTION

Chapter 21 addressed the nature and sources of hazardous wastes and their environmental chemistry and pointed out some of the major problems associated with such wastes. Chapter 22 deals with means for minimizing wastes, utilizing materials that might go into wastes, and treating and disposing of wastes, the generation of which cannot be avoided. The practice of industrial ecology combined with green chemistry is all about not producing wastes and, instead, utilizing wastes for useful purposes. Therefore, in dealing with wastes, it is essential in the modern age to consider the potential contribution of industrial ecology.

Since the 1970s, efforts to reduce and clean up hazardous wastes have been characterized by:

- Legislation
- Regulation
- Litigation
- Procrastination
- Modeling
- Analysis
- Cleanup of a few select sites

It is perhaps fair to say that in proportion to the magnitude of the problems and the amount of money devoted to them so far, insufficient progress has been made in coping with hazardous wastes. In the U.S., huge amounts of time have been devoted to promulgating hazardous-waste regulations, instrument manufacturers have prospered as more and more chemical analyses have been required, and computationists, some of whom would be offended at the sight of any chemical, much less a hazardous one, have consumed thousands of hours of computer time to model hazardous-waste systems. This is to say nothing of the vast expense of litigation that has gone into lawsuits dealing with hazardous-waste sites. In the future, a higher percentage of

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the effort and resources devoted to hazardous wastes needs to be placed on remediation of existing problems and preventive action to avoid future problems.

The U. S. Superfund act, a particular target of criticism by industrial and other groups, has been under consideration for renewal each year since 1994. A total of nine bills dealing with Superfund were introduced in the U.S. Congress in 1999, none with much of a chance of passing.[1] Critics contend that Superfund's efforts have been directed toward high-cost solutions for minimal risks. Many Superfund critics contend that a much greater emphasis must be placed on institutional controls and waste isolation to deal effectively with improperly disposed hazardous wastes.

This chapter discusses how environmental chemistry can be applied to hazardous-waste management to develop measures by which chemical wastes can be minimized, recycled, treated, and disposed. In descending order of desirability, hazardous-waste management attempts to accomplish the following:

- Do not produce it
- If making it cannot be avoided, produce only minimum quantities
- Recycle it
- If it is produced and cannot be recycled, treat it, preferably in a way that makes it nonhazardous
- If it cannot be rendered nonhazardous, dispose of it in a safe manner
- Once it is disposed, monitor it for leaching and other adverse effects

The **effectiveness** of a hazardous-waste management system is a measure of how well it reduces the quantities and hazards of wastes. As shown in Figure 22.1, the best management option consists of measures that prevent generation of wastes. Next in order of desirability is recovery and recycling of waste constituents, followed by destruction and treatment with conversion to nonhazardous-waste forms. The least desirable option is disposal of hazardous materials in storage or landfill.

22.2 WASTE REDUCTION AND MINIMIZATION

The initial sections of this chapter address waste reduction and minimization. During recent years, substantial efforts have been made toward reducing the quantities of wastes and, therefore, the burden of dealing with wastes. Much of this effort has been the result of legislation and regulations restricting wastes, along with the resulting concerns over possible legal actions and lawsuits. In many cases—and ideally in all—minimizing the quantities of wastes produced is simply good business. Wastes are materials, materials have value and, therefore, all materials should be used for some beneficial purpose and not discarded as wastes, usually at a high cost for waste disposal.

Industrial ecology is all about the efficient use of materials. Therefore, by its nature, a system of industrial ecology is also a system of waste reduction and minimization. In reducing quantities of wastes, it is important to take the broadest possible view. This is because dealing with one waste problem in isolation may simply create another. Early efforts to control air and water pollution resulted in

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problems from hazardous wastes isolated from industrial operations. A key aspect of industrial ecology is its approach based upon industrial systems as a whole, making a system of industrial ecology by far the best means of dealing with wastes by avoiding their production.

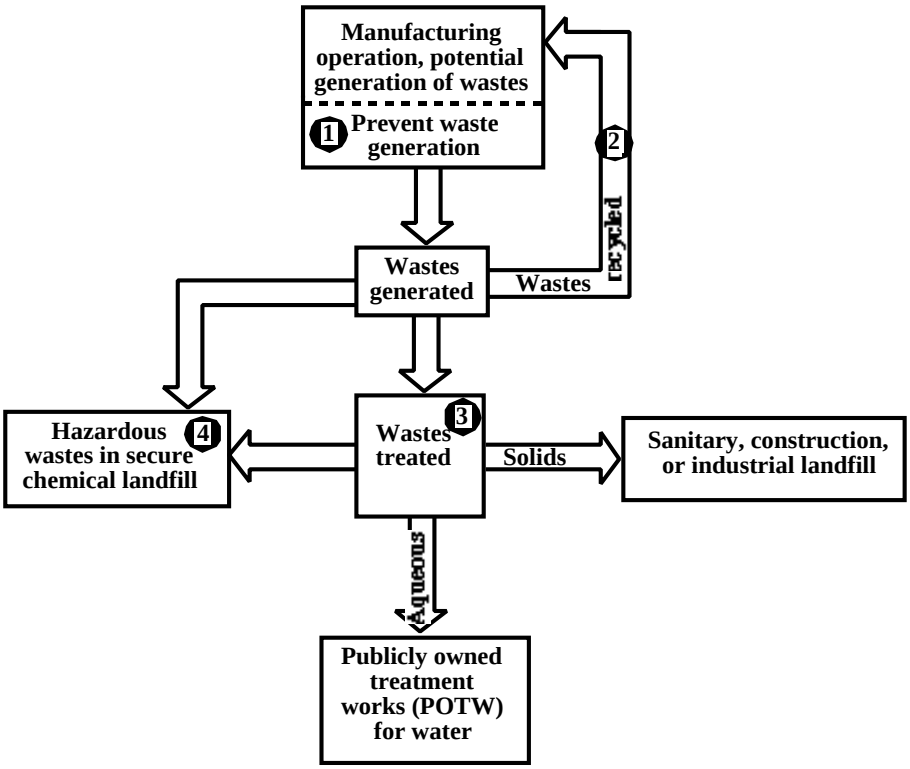


Figure 22.1 Order of effectiveness of waste-treatment management options. The darkened circles indicate the degree of effectiveness from the most desirable (1) to the least (4).

Many hazardous-waste problems can be avoided at early stages by **waste reduction** (cutting down quantities of wastes from their sources) and **waste minimization** (utilization of treatment processes that reduce the quantities of wastes requiring ultimate disposal). This section outlines basic approaches to waste minimization and reduction.

There are several ways in which quantities of wastes can be reduced, including source reduction, waste separation and concentration, resource recovery, and waste recycling. The most effective approaches to minimizing wastes center around careful control of manufacturing processes, taking into consideration discharges and the potential for waste minimization at every step of manufacturing. Viewing the process as a whole (as outlined for a generalized chemical manufacturing process in Figure 22.2) often enables crucial identification of the source of a waste, such as a raw material impurity, catalyst, or process solvent. Once a source is identified, it is much easier to take measures to eliminate or reduce the waste. The most effective approach to minimizing wastes is to emphasize waste minimization as an integral part of plant design.[2]

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Modifications of the manufacturing process can yield substantial waste reduction. Some such modifications are of a chemical nature. Changes in chemical reaction conditions can minimize production of by-product hazardous substances. In some cases, potentially hazardous catalysts, such as those formulated from toxic substances, can be replaced by catalysts that are nonhazardous or that can be recycled rather than discarded. Wastes can be minimized by volume reduction, for example through dewatering and drying sludge.

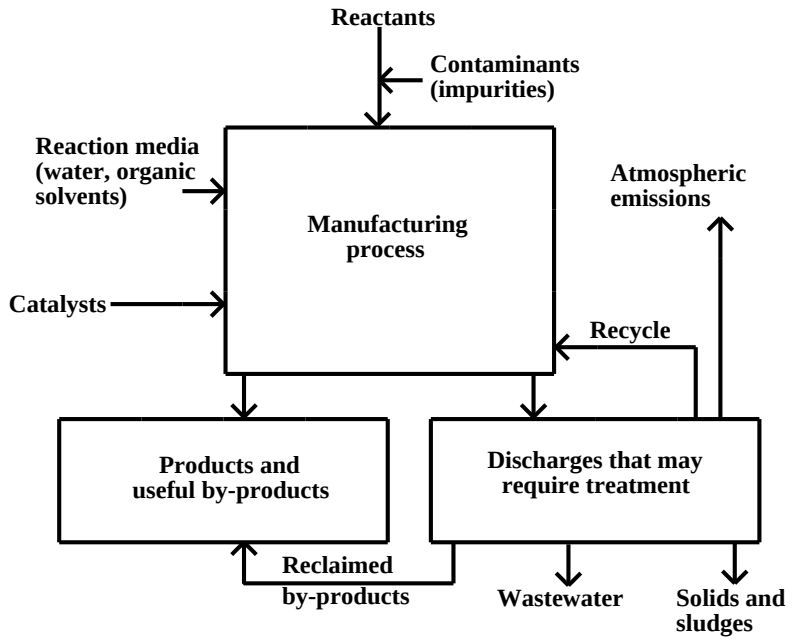


Figure 22.2 Chemical manufacturing process from the viewpoint of discharges and waste minimization.

Many kinds of waste streams are candidates for minimization. As examples, such waste streams identified at U.S. Government federal facilities have included solvents used for cleaning and degreasing, spent motor oil from gasoline and diesel engines, leftover and waste paint thinners, antifreeze/antiboil engine cooling formulations, batteries, inks, exposed photographic film, and pathology wastes.[3] The sources of the wastes are as varied as the waste streams themselves. Motor pool maintenance garages generate used motor oil and spent coolants. Hospitals, clinics, and medical laboratories generate pathology wastes. Aircraft maintenance depots where aircraft are cleaned, chemically stripped of paint and coatings, repainted, and electroplated generate large quantities of effluents, including organic materials.[4] Other facilities generating wastes include equipment- and arms-maintenance facilities, photo developing and printing laboratories, paint shops, and arts and crafts shops.

A crucial part of the process for reducing and minimizing wastes is the development of a material balance, which is an integral part of the practice of industrial ecology.[5] Such a balance addresses various aspects of waste streams, including sources, identification, and quantities of wastes and methods and costs of handling,

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treatment, recycling, and disposal. Priority waste streams can then be subjected to detailed process investigations to obtain the information needed to reduce wastes.

There are encouraging signs of progress in the area of waste minimization. All major companies have initiated programs to minimize quantities of wastes produced. A typical success story is a 97% reduction of landfill wastes from Mobil's Torrance petroleum refinery from 1989 to 1993. During the same period, the refinery went from less than 1% waste recycle to more than 70%. One of the technologies used for waste reduction was the Mobil Oil Sludge Coking Process.[6] Similar success stories in reducing wastes can be cited by a number of concerns in the U.S. and throughout the world.

22.3 RECYCLING

Wherever possible, recycling and reuse should be accomplished on-site because it avoids having to move wastes, and because a process that produces recyclable materials is often the most likely to have use for them. The four broad areas in which something of value can be obtained from wastes are the following:

- Direct recycle as raw material to the generator, as with the return to feed-stock of raw materials not completely consumed in a synthesis process
- Transfer as a raw material to another process; a substance that is a waste product from one process may serve as a raw material for another, sometimes in an entirely different industry
- Utilization for pollution control or waste treatment, such as use of waste alkali to neutralize waste acid
- Recovery of energy, for example, from the incineration of combustible hazardous wastes

Examples of Recycling

Recycling of scrap industrial impurities and products occurs on a large scale with a number of different materials. Most of these materials are not hazardous but, as with most large-scale industrial operations, their recycling may involve the use or production of hazardous substances. Some of the more important examples are the following:

- **Ferrous metals** composed primarily of iron and used largely as feedstock for electric-arc furnaces
- **Nonferrous metals**, including aluminum (which ranks next to iron in terms of quantities recycled), copper and copper alloys, zinc, lead, cadmium, tin, silver, and mercury
- **Metal compounds**, such as metal salts
- **Inorganic substances** including alkaline compounds (such as sodium hydroxide used to remove sulfur compounds from petroleum products),

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acids (steel pickling liquor where impurities permit reuse), and salts (for example, ammonium sulfate from coal coking used as fertilizer)

- **Glass**, which makes up about 10 % of municipal refuse
- **Paper**, commonly recycled from municipal refuse
- **Plastic**, consisting of a variety of moldable polymeric materials and composing a major constituent of municipal wastes
- **Rubber**
- **Organic substances**, especially solvents and oils, such as hydraulic and lubricating oils
- **Catalysts** from chemical synthesis or petroleum processing
- Materials with **agricultural uses**, such as waste lime or phosphate-containing sludges used to treat and fertilize acidic soils

Waste Oil Utilization and Recovery

Waste oil generated from lubricants and hydraulic fluids is one of the more commonly recycled materials. Annual production of waste oil in the U.S. is of the order of 4 billion liters. Around half of this amount is burned as fuel and lesser quantities are recycled or disposed of as waste. The collection, recycling, treatment, and disposal of waste oil are all complicated by the fact that it comes from diverse, widely dispersed sources and contains several classes of potentially hazardous contaminants. These are divided between organic constituents (polycyclic aromatic hydrocarbons, chlorinated hydrocarbons) and inorganic constituents (aluminum, chromium, and iron from wear of metal parts; barium and zinc from oil additives; lead from leaded gasoline).

Recycling Waste Oil

The processes used to convert waste oil to a feedstock hydrocarbon liquid for lubricant formulation are illustrated in Figure 22.3. The first of these uses distillation to remove water and light ends that have come from condensation and contaminant fuel. The second, or processing, step may be a vacuum distillation in which the three

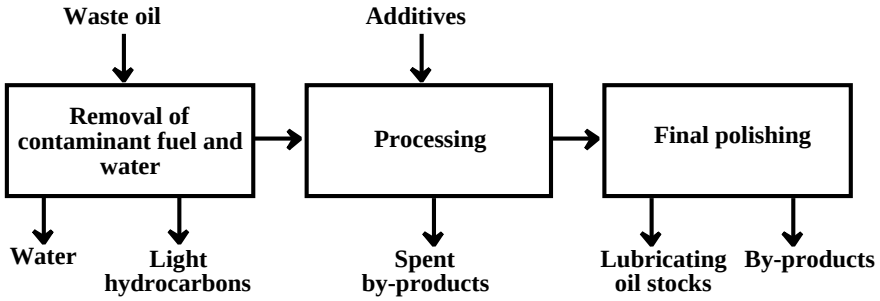


Figure 22.3 Major steps in reprocessing waste oil.

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products are oil for further processing, a fuel oil cut, and a heavy residue. The processing step may also employ treatment with a mixture of solvents including isopropyl and butyl alcohols and methylethyl ketone to dissolve the oil and leave contaminants as a sludge; or contact with sulfuric acid to remove inorganic contaminants followed by treatment with clay to take out acid and contaminants that cause odor and color. The third step shown in Figure 22.3 employs vacuum distillation to separate lubricating oil stocks from a fuel fraction and heavy residue. This phase of treatment may also involve hydrofinishing, treatment with clay, and filtration.

Waste Oil Fuel

For economic reasons, waste oil that is to be used for fuel is given minimal treatment of a physical nature, including settling, removal of water, and filtration. Metals in waste fuel oil become highly concentrated in its fly ash, which may be hazardous.

Waste Solvent Recovery and Recycle

The recovery and recycling of waste solvents has some similarities to the recycling of waste oil and is also an important enterprise. Among the many solvents listed as hazardous wastes and recoverable from wastes are dichloromethane, tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, benzene, liquid alkanes, 2-nitropropane, methylisobutyl ketone, and cyclohexanone. For reasons of both economics and pollution control, many industrial processes that use solvents are equipped for solvent recycle. The basic scheme for solvent reclamation and reuse is shown in Figure 22.4.

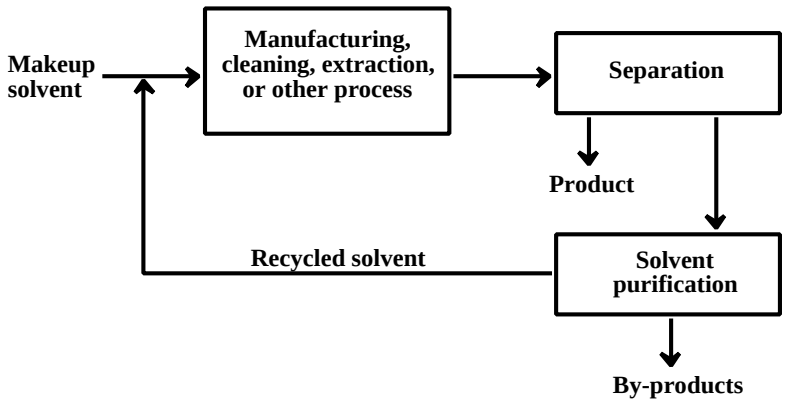


Figure 22.4 Overall process for recycling solvents.

A number of operations are used in solvent purification. Entrained solids are removed by settling, filtration, or centrifugation. Drying agents may be used to remove water from solvents, and various adsorption techniques and chemical treatment may be required to free the solvent from specific impurities. Fractional distillation, often requiring several distillation steps, is the most important operation in solvent purification and recycling. It is used to separate solvents from impurities, water, and other solvents.

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Recovery of Water from Wastewater

It is often desirable to reclaim water from wastewater.[7] This is especially true in regions where water is in short supply. Even where water is abundant, water recycling is desirable to minimize the amount of water that is discharged.

A little more than half of the water used in the U.S. is consumed by agriculture, primarily for irrigation. Steam-generating power plants consume about one-fourth of the water, and other uses, including manufacturing and domestic uses, account for the remainder.

The three major manufacturing consumers of water are chemicals and allied products, paper and allied products, and primary metals. These industries use water for cooling, processing, and boilers. Their potential for water reuse is high and their total consumption of water is projected to drop in future years as recycling becomes more common.

The degree of treatment required for reuse of wastewater depends upon the water's intended use. Water used for industrial quenching and washing usually requires the least treatment, and wastewater from some other processes may be suitable for these purposes without additional treatment. At the other end of the scale, boiler makeup water, potable (drinking) water, water used to directly recharge aquifers, and water that people will directly contact (in boating, water skiing, and similar activities) must be of very high quality.

The treatment processes applied to wastewater for reuse and recycle depend upon both the characteristics of the wastewater and its intended uses. Solids can be removed by sedimentation and filtration. Biochemical oxygen demand is reduced by biological treatment, including trickling filters and activated sludge treatment. For uses conducive to the growth of nuisance algae, nutrients may have to be removed. The easiest of these to handle is nutrient phosphate, which can be precipitated with lime. Nitrogen can be removed by denitrification processes.

Two of the major problems with industrial water recycling are heavy metals and dissolved toxic organic species. Heavy metals may be removed by ion exchange or precipitation by base or sulfide. The organic species are usually removed with activated carbon filtration. Some organic species are biologically degraded by bacteria in biological wastewater treatment.

One of the greater sources of potentially hazardous wastewater arises from oil–water separators at wash racks where manufactured parts and materials are washed. Because of the use of surfactants and solvents in the washwater, the separated water tends to contain emulsified oil that is incompletely separated in an oil–water separator. In addition, the sludge that accumulates at the bottom of the separator may contain hazardous constituents, including heavy metals and some hazardous organic constituents. Several measures that include the incorporation of good industrial ecology practice can be taken to eliminate these problems.[8] One such measure is to eliminate the use of surfactants and solvents that tend to contaminate the water, and to use surfactants and solvents that are more amenable to separation and treatment. Another useful measure is to treat the water to remove harmful constituents and recycle it. This not only conserves water and reduces disposal costs, but also enables recycling of surfactants and other additives.

The ultimate water quality is achieved by processes that remove solutes from water, leaving pure H_2O. A combination of activated carbon treatment to remove

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organics, cation exchange to remove dissolved cations, and anion exchange for dissolved anions can provide very high–quality water from wastewater. Reverse osmosis (see Chapter 8) can accomplish the same objective. However, these processes generate spent activated carbon, ion exchange resins that require regeneration, and concentrated brines (from reverse osmosis) that require disposal, all of which have the potential to end up as hazardous wastes.

22.4 PHYSICAL METHODS OF WASTE TREATMENT

This section addresses predominantly physical methods for waste treatment and the following section addresses methods that utilize chemical processes. It should be kept in mind that most waste treatment measures have both physical and chemical aspects. The appropriate treatment technology for hazardous wastes obviously depends upon the nature of the wastes. These may consist of volatile wastes (gases, volatile solutes in water, gases or volatile liquids held by solids, such as catalysts), liquid wastes (wastewater, organic solvents), dissolved or soluble wastes (water-soluble inorganic species, water-soluble organic species, compounds soluble in organic solvents), semisolids (sludges, greases), and solids (dry solids, including granular solids with a significant water content, such as dewatered sludges, as well as solids suspended in liquids). The type of physical treatment to be applied to wastes depends strongly upon the physical properties of the material treated, including state of matter, solubility in water and organic solvents, density, volatility, boiling point, and melting point.

As shown in Figure 22.5, waste treatment may occur at three major levels—**primary**, **secondary**, and **polishing**—somewhat analogous to the treatment of wastewater (see Chapter 8). Primary treatment is generally regarded as preparation for further treatment, although it can result in the removal of byproducts and reduction of the quantity and hazard of the waste. Secondary treatment detoxifies, destroys, and removes hazardous constituents. Polishing usually refers to treatment of water that is removed from wastes so that it can be safely discharged. However, the term can be broadened to apply to the treatment of other products as well so that they can be safely discharged or recycled.

Methods of Physical Treatment

Knowledge of the physical behavior of wastes has been used to develop various unit operations for waste treatment that are based upon physical properties. These operations include the following:

- Phase separation
 - Filtration
- Phase transition
 - Distillation
 - Evaporation
 - Physical precipitation
- Phase transfer
 - Extraction
 - Sorption
- Membrane separations
 - Reverse osmosis
 - Hyper- and ultrafiltration

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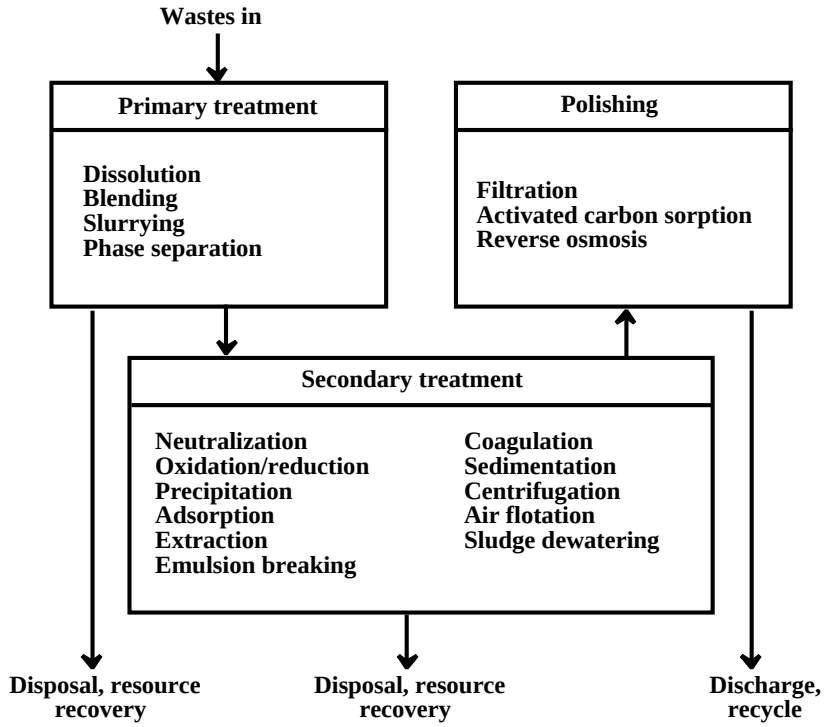


Figure 22.5 Major phases of waste treatment.

Phase Separations

The most straightforward means of physical treatment involves separation of components of a mixture that are already in two different phases. **Sedimentation** and **decanting** are easily accomplished with simple equipment. In many cases the separation must be aided by mechanical means, particularly **filtration** or **centrifugation**. **Flotation** is used to bring suspended organic matter or finely divided particles to the surface of a suspension. In the process of **dissolved air flotation** (DAF), air is dissolved in the suspending medium under pressure and comes out of solution when the pressure is released as minute air bubbles attached to suspended particles, which causes the particles to float to the surface.

An important and often difficult waste-treatment step is **emulsion breaking**, in which colloidal-sized **emulsions** are caused to aggregate and settle from suspension. Agitation, heat, acid, and the addition of **coagulants** consisting of organic polyelectrolytes, or inorganic substances such as an aluminum salt, can be used for this purpose. The chemical additive acts as a flocculating agent to cause the particles to stick together and settle out.

Phase Transition

A second major class of physical separation is that of **phase transition** in which a material changes from one physical phase to another. It is best exemplified by

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distillation, which is used in treating and recycling solvents, waste oil, aqueous phenolic wastes, xylene contaminated with paraffin from histological laboratories, and mixtures of ethylbenzene and styrene. Distillation produces **distillation bottoms** (still bottoms), which are often hazardous and polluting. These consist of unevaporated solids, semisolid tars, and sludges from distillation. Specific examples with their hazardous-waste numbers are distillation bottoms from the production of acetaldehyde from ethylene (hazardous-waste number K009), and still bottoms from toluene reclamation distillation in the production of disulfoton (K036). The landfill disposal of these and other hazardous distillation bottoms used to be widely practiced but is now severely limited.

Evaporation is usually employed to remove water from an aqueous waste to concentrate it. A special case of this technique is **thin-film evaporation** in which volatile constituents are removed by heating a thin layer of liquid or sludge waste spread on a heated surface.

Drying—removal of solvent or water from a solid or semisolid (sludge) or the removal of solvent from a liquid or suspension—is a very important operation because water is often the major constituent of waste products, such as sludges obtained from emulsion breaking. In **freeze drying**, the solvent, usually water, is sublimed from a frozen material. Hazardous-waste solids and sludges are dried to reduce the quantity of waste, to remove solvent or water that might interfere with subsequent treatment processes, and to remove hazardous volatile constituents. Dewatering can often be improved with addition of a filter aid, such as diatomaceous earth, during the filtration step.

Stripping is a means of separating volatile components from less volatile ones in a liquid mixture by the partitioning of the more volatile materials to a gas phase of air or steam (steam stripping). The gas phase is introduced into the aqueous solution or suspension containing the waste in a stripping tower that is equipped with trays or packed to provide maximum turbulence and contact between the liquid and gas phases. The two major products are condensed vapor and a stripped bottoms residue. Examples of two volatile components that can be removed from water by air stripping are benzene and dichloromethane. Air stripping can also be used to remove ammonia from water that has been treated with a base to convert ammonium ion to volatile ammonia.

Physical precipitation is used here as a term to describe processes in which a solid forms from a solute in solution as a result of a physical change in the solution, as compared with chemical precipitation (see Section 22.5), in which a chemical reaction in solution produces an insoluble material. The major changes that can cause physical precipitation are cooling the solution, evaporation of solvent, or alteration of solvent composition. The most common type of physical precipitation by alteration of solvent composition occurs when a water-miscible organic solvent is added to an aqueous solution so that the solubility of a salt is lowered below its concentration in the solution.

Phase Transfer

Phase transfer consists of the transfer of a solute in a mixture from one phase to another. An important type of phase transfer process is **solvent extraction**, a process

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in which a substance is transferred from solution in one solvent (usually water) to another (usually an organic solvent) without any chemical change taking place. When solvents are used to leach substances from solids or sludges, the process is called **leaching**. Solvent extraction and the major terms applicable to it are summarized in Figure 22.6. The same terms and general principles apply to leaching. The major application of solvent extraction to waste treatment has been in the removal of phenol from by-product water produced in coal coking, petroleum refining, and chemical syntheses that involve phenol.

One of the more promising approaches to solvent extraction and leaching of hazardous wastes is the use of **supercritical fluids**, most commonly CO_2, as extraction solvents. As discussed in Chapter 20, Section 20.7, a supercritical fluid is a substance above its critical temperature and pressure (31.1˚C and 73.8 atm, respectively, for CO_2) with characteristics of both liquid and gas. After a substance has been extracted from a waste into a supercritical fluid, the pressure can be released, resulting in separation of the substance extracted. The fluid can then be compressed again and recirculated through the extraction system. Some possibilities for treatment of hazardous wastes by extraction with supercritical CO_2 include removal of organic contaminants from wastewater, extraction of organohalide pesticides from soil, extraction of oil from emulsions used in aluminum and steel processing, and regeneration of spent activated carbon. Waste oils contaminated with PCBs, metals, and water can be purified using supercritical ethane.

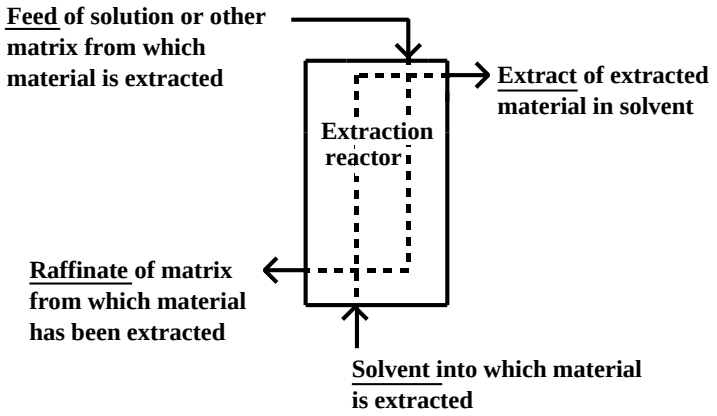


Figure 22.6 Outline of solvent extraction/leaching process with important terms underlined.

Transfer of a substance from a solution to a solid phase is called **sorption**. The most important sorbent is **activated carbon** used for several purposes in waste treatment; in some cases it is adequate for complete treatment. It can also be applied to pretreatment of waste streams going into processes such as reverse osmosis to improve treatment efficiency and reduce fouling. Effluents from other treatment processes, such as biological treatment of degradable organic solutes in water, can be polished with activated carbon. Activated carbon sorption is most effective for removing from water those hazardous-waste materials that are poorly water-soluble and that have high molar masses, such as xylene, naphthalene (U165), cyclohexane (U056); chlorinated hydrocarbons, phenol (U188), aniline (U012), dyes, and surfac-

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tants. Activated carbon does not work well for organic compounds that are highly water-soluble or polar.

Solids other than activated carbon can be used for sorption of contaminants from liquid wastes. These include synthetic resins composed of organic polymers and mineral substances. Of the latter, clay is employed to remove impurities from waste lubricating oils in some oil recycling processes.

Molecular Separation

A third major class of physical separation is **molecular separation**, often based upon **membrane processes** in which dissolved contaminants or solvent pass through a size-selective membrane under pressure. The products are a relatively pure solvent phase (usually water) and a concentrate enriched in the solute impurities. **Hyperfiltration** allows passage of species with molecular masses of about 100 to 500, whereas **ultrafiltration** is used for the separation of organic solutes with molar masses of 500 to 1,000,000. With both of these techniques, water and lower molar mass solutes under pressure pass through the membrane as a stream of purified **permeate**, leaving behind a stream of **concentrate** containing impurities in solution or suspension. Ultrafiltration and hyperfiltration are especially useful for concentrating suspended oil, grease, and fine solids in water. They also serve to concentrate solutions of large organic molecules and heavy metal ion complexes.

Reverse osmosis is the most widely used of the membrane techniques. Although superficially similar to ultrafiltration and hyperfiltration, it operates on a different principle in that the membrane is selectively permeable to water and excludes ionic solutes. Reverse osmosis uses high pressures to force permeate through the membrane, producing a concentrate containing high levels of dissolved salts.

Electrodialysis, sometimes used to concentrate plating wastes, employs membranes alternately permeable to cations and to anions. The driving force for the separation is provided by electrolysis with a direct current between two electrodes. Alternate layers between the membranes contain concentrate (brine) and purified water.

22.5 CHEMICAL TREATMENT: AN OVERVIEW

The applicability of chemical treatment to wastes depends upon the chemical properties of the waste constituents, particularly acid-base, oxidation-reduction, precipitation, and complexation behavior; reactivity; flammability/combustibility; corrosivity; and compatibility with other wastes. The chemical behavior of wastes translates to various unit operations for waste treatment that are based upon chemical properties and reactions. These include the following:

- Acid-base neutralization
- Chemical precipitation
- Chemical extraction and leaching
- Oxidation
- Ion exchange
- Reduction

Some of the more sophisticated means available for treatment of wastes have been developed for pesticide disposal.

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Acid-Base Neutralization

Waste acids and bases are treated by **neutralization**:

$$H^+ + OH^- \rightarrow H_2O \quad (22.5.1)$$

Although simple in principle, neutralization can present some problems in practice. These include evolution of volatile contaminants, mobilization of soluble substances, excessive heat generated by the neutralization reaction, and corrosion to apparatus. By adding too much or too little of the neutralizing agent, it is possible to get a product that is too acidic or basic. Lime, $Ca(OH)_2$, is widely used as a base for treating acidic wastes. Because of lime's limited solubility, solutions of excess lime do not reach extremely high pH values. Sulfuric acid, H_2SO_4, is a relatively inexpensive acid for treating alkaline wastes. However, addition of too much sulfuric acid can produce highly acidic products; for some applications, acetic acid CH_3COOH, is preferable. As noted above, acetic acid is a weak acid and an excess of it does little harm. It is also a natural product and biodegradable.

Neutralization, or pH adjustment, is often required prior to the application of other waste treatment processes. Processes that may require neutralization include oxidation-reduction, activated carbon sorption, wet air oxidation, stripping, and ion exchange. Microorganisms usually require a pH in the range of 6–9, so neutralization may be required prior to biochemical treatment.

Chemical Precipitation

Chemical precipitation is used in hazardous-waste treatment primarily for the removal of heavy-metal ions from water as shown below for the chemical precipitation of cadmium:

$$Cd^{2+}(aq) + HS^-(aq) \rightarrow CdS(s) + H^+(aq) \quad (22.5.2)$$

Precipitation of Metals

The most widely used means of precipitating metal ions is by the formation of hydroxides such as chromium(III) hydroxide:

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3 \quad (22.5.3)$$

The source of hydroxide ion is a base (alkali), such as lime ($Ca(OH)_2$), sodium hydroxide (NaOH), or sodium carbonate (Na_2CO_3). Most metal ions tend to produce basic salt precipitates, such as basic copper(II) sulfate, $CuSO_4 \cdot 3Cu(OH)_2$, which is formed as a solid when hydroxide is added to a solution containing Cu^{2+} and SO_4^{2-} ions. The solubilities of many heavy metal hydroxides reach a minimum value, often at a pH in the range of 9–11, then increase with increasing pH values due to the formation of soluble hydroxo complexes, as illustrated by the following reaction:

$$Zn(OH)_2(s) + 2OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq) \quad (22.5.4)$$

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The chemical precipitation method that is used most is precipitation of metals as hydroxides and basic salts with lime. Sodium carbonate can be used to precipitate metal hydroxides ($Fe(OH)_3 \cdot xH_2O$) carbonates ($CdCO_3$), or basic carbonate salts ($2PbCO_3 \cdot Pb(OH)_2$). The carbonate anion produces hydroxide by virtue of its hydrolysis reaction with water:

$$CO_3^{2-} + H_2O \rightarrow HCO_3^- + OH^- \quad (22.5.5)$$

Carbonate, alone, does not give as high a pH as do alkali metal hydroxides, which may have to be used to precipitate metals that form hydroxides only at relatively high pH values.

The solubilities of some heavy metal sulfides are extremely low, so precipitation by H_2S or other sulfides (see Reaction 22.5.2) can be a very effective means of treatment. Hydrogen sulfide is a toxic gas that is itself considered to be a hazardous waste (U135). Iron(II) sulfide (ferrous sulfide) can be used as a safe source of sulfide ion to produce sulfide precipitates with other metals that are less soluble than FeS. However, toxic H_2S can be produced when metal sulfide wastes contact acid:

$$MS + 2H^+ \rightarrow M^{2+} + H_2S \quad (22.5.6)$$

Some metals can be precipitated from solution in the elemental metal form by the action of a reducing agent such as sodium borohydride,

$$4Cu^{2+} + NaBH_4 + 2H_2O \rightarrow 4Cu + NaBO_2 + 8H^+ \quad (22.5.7)$$

or with more active metals in a process called **cementation**:

$$Cd^{2+} + Zn \rightarrow Cd + Zn^{2+} \quad (22.5.8)$$

Regardless of the method used to precipitate a metal, the form of the metal in the waste solution can be an important consideration. Chelated metals can be especially difficult to remove. For example, difficulties encountered in precipitating copper from waste printed circuit board formulations revealed that chelation of the copper by EDTA chelant was responsible for the problem.[9]

Coprecipitation of Metals

In some cases, advantage may be taken of the phenomenon of coprecipitation to remove metals from wastes. A good example of this application is the coprecipitation of lead from battery industry wastewater with iron(III) hydroxide. Raising the pH of such a wastewater consisting of dilute sulfuric acid and contaminated with Pb^{2+} ion precipitates lead as several species, including $PbSO_4$, $Pb(OH)_2$, and $Pb(OH)_2 \cdot 2PbCO_3$. In the presence of iron(III), gelatinous $Fe(OH)_3$ forms, which coprecipitates the lead, leading to much lower values of lead concentration than would otherwise be possible. Effective removal of lead from battery industry wastewater to below 0.2 ppm has been achieved by first adding an optimum quantity of iron(III), adjustment of the pH to a range of 9–9.5, addition of a polyelectrolyte to aid coagulation, and filtration.[10]

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Oxidation/Reduction

As shown by the reactions in Table 22.1, **oxidation** and **reduction** can be used for the treatment and removal of a variety of inorganic and organic wastes. Some waste oxidants can be used to treat oxidizable wastes in water and cyanides. Ozone, O_3, is a strong oxidant that can be generated on-site by an electrical discharge through dry air or oxygen. Ozone employed as an oxidant gas at levels of 1–2 wt% in air and 2–5 wt% in oxygen has been used to treat a large variety of oxidizable contaminants, effluents, and wastes including wastewater and sludges containing oxidizable constituents.

Table 22.1 Oxidation-Reduction Reactions Used to Treat Wastes

Waste Substance	Reaction with Oxidant or Reductant
Oxidation of Organics	
Organic matter $\{CH_2O\}$	$\{CH_2O\} + 2\{O\} \rightarrow CO_2 + H_2O$
Aldehyde	$CH_3CHO + \{O\} \rightarrow CH_3COOH$ (acid)
Oxidation of Inorganics	
Cyanide	$2CN^- + 5OCl^- + H_2O \rightarrow N_2 + 2HCO_3^- + 5Cl^-$
Iron(II)	$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+$
Sulfur dioxide	$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4$
Reduction of Inorganics	
Chromate	$2CrO_4^{2-} + 3SO_2 + 4H^+ \rightarrow Cr_2(SO_4)_3 + 2H_2O$
Permanganate	$MnO_4^- + 3Fe^{2+} + 7H_2O \rightarrow MnO_2(s) + 3Fe(OH)_3(s) + 5H^+$

Electrolysis

As shown in Figure 22.7, **electrolysis** is a process in which one species in solution (usually a metal ion) is reduced by electrons at the **cathode** and another gives up electrons to the **anode** and is oxidized there. In hazardous-waste applications, electrolysis is most widely used in the recovery of cadmium, copper, gold, lead, silver, and zinc. Metal recovery by electrolysis is made more difficult by the presence of cyanide ion, which stabilizes metals in solution as the cyanide complexes, such as $Ni(CN)_4^{2-}$.

Electrolytic removal of contaminants from solution can be by direct electro-deposition, particularly of reduced metals, and as the result of secondary reactions of

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electrolytically generated precipitating agents. A specific example of both is the electrolytic removal of both cadmium and nickel from wastewater contaminated by nickel/cadmium battery manufacture using fibrous carbon electrodes.[11] At the cathode, cadmium is removed directly by reduction to the metal:

$$Cd^{2+} + 2e^- \rightarrow Cd \qquad (22.5.9)$$

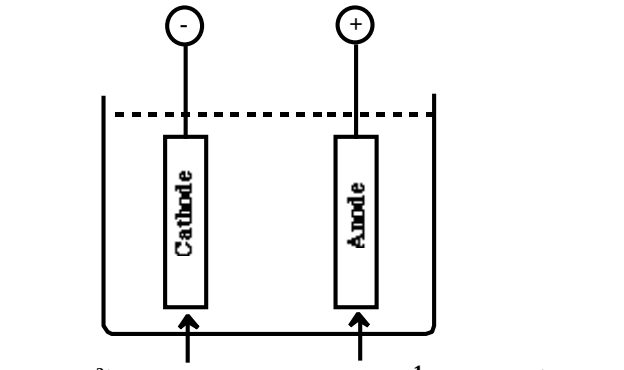


Figure 22.7 Electrolysis of copper solution.

At relatively high cathodic potentials, hydroxide is formed by the electrolytic reduction of water,

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad (22.5.10)$$

or by the reduction of molecular oxygen, if it is present:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \qquad (22.5.11)$$

If the localized pH at the cathode surface becomes sufficiently high, cadmium can be precipitated and removed as colloidal $Cd(OH)_2$. The direct electrodeposition of nickel is too slow to be significant, but it is precipitated as solid $Ni(OH)_2$ at pH values above 7.5.

Cyanide, which is often present as an ingredient of electroplating baths with metals such as cadmium and nickel, can be removed by oxidation with electrolytically generated elemental chlorine at the anode. Chlorine is generated by the anodic oxidation of added chloride ion:

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad (22.5.12)$$

The electrolytically generated chlorine then breaks down cyanide by a series of reactions for which the overall reaction is the following:

$$2CN^- + 5Cl_2 + 8OH^- \rightarrow 10Cl^- + N_2 + 2CO_2 + 4H_2O \qquad (22.5.13)$$

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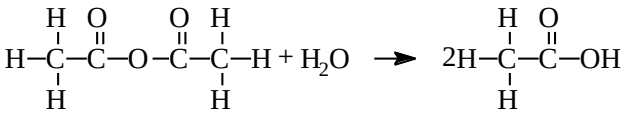
Hydrolysis

One of the ways to dispose of chemicals that are reactive with water is to allow them to react with water under controlled conditions, a process called **hydrolysis**. Inorganic chemicals that can be treated by hydrolysis include metals that react with water; metal carbides, hydrides, amides, alkoxides, and halides; and nonmetal oxyhalides and sulfides. Examples of the treatment of these classes of inorganic species are given in Table 22.2.

Table 22.2 Inorganic Chemicals That Can Be Treated by Hydrolysis

Class of chemical	Reaction with oxidant or reductant
Active metals (calcium)	$Ca + 2H_2O \rightarrow H_2 + Ca(OH)_2$
Hydrides (sodium aluminum hydride)	$NaAlH_4 + 4H_2O \rightarrow 4H_2 + NaOH + Al(OH)_3$
Carbides (calcium carbide)	$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$
Amides (sodium amide)	$NaNH_2 + H_2O \rightarrow NaOH + NH_3$
Halides (silicon tetrachloride)	$SiCl_4 + 2H_2O \rightarrow SiO_2 + 4HCl$
Alkoxides (sodium ethoxide)	$NaOC_2H_5 + H_2O \rightarrow NaOH + C_2H_5OH$

Organic chemicals can also be treated by hydrolysis. For example, toxic acetic anhydride is hydrolyzed to relatively safe acetic acid:



Acetic anhydride
(an acid anhydride)

(22.5.9)

Chemical Extraction and Leaching

Chemical extraction or **leaching** in hazardous-waste treatment is the removal of a hazardous constituent by chemical reaction with an extractant in solution. Poorly soluble heavy metal salts can be extracted by reaction of the salt anions with H^+ as illustrated by the following:

$$PbCO_3 + H^+ \rightarrow Pb^{2+} + HCO_3^- \qquad (22.5.10)$$

Acids also dissolve basic organic compounds such as amines and aniline. Extraction with acids should be avoided if cyanides or sulfides are present to prevent formation

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of toxic hydrogen cyanide or hydrogen sulfide. Nontoxic weak acids are usually the safest to use. These include acetic acid, CH_3COOH, and the acid salt, NaH_2PO_4.

Chelating agents, such as dissolved ethylenediaminetetraacetate (EDTA, HY^{3-}), dissolve insoluble metal salts by forming soluble species with metal ions:

$$FeS + HY^{3-} \rightarrow FeY^{2-} + HS^{-} \qquad (22.5.11)$$

Heavy-metal ions in soil contaminated by hazardous wastes may be present in a coprecipitated form with insoluble iron(III) and manganese(IV) oxides, Fe_2O_3 and MnO_2, respectively. These oxides can be dissolved by reducing agents, such as solutions of sodium dithionate/citrate or hydroxylamine. This results in the production of soluble Fe^{2+} and Mn^{2+} and the release of heavy-metal ions, such as Cd^{2+} or Ni^{2+}, which are removed with the water.

Ion Exchange

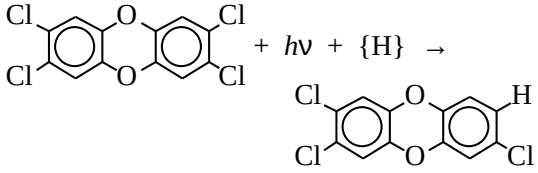
Ion exchange is a means of removing cations or anions from solution onto a solid resin, which can be regenerated by treatment with acids, bases, or salts. The greatest use of ion exchange in hazardous-waste treatment is for the removal of low levels of heavy-metal ions from wastewater:

$$2H^{+}\text{-}\{CatExchr\} + Cd^{2+} \rightarrow Cd^{2+}\text{-}\{CatExchr\}_2 + 2H^{+} \qquad (22.5.12)$$

Ion exchange is used in the metal plating industry to purify rinsewater and spent plating bath solutions. Cation exchangers remove cationic metal species, such as Cu^{2+}, from such solutions. Anion exchangers remove anionic cyanide metal complexes such as $Ni(CN)_4^{2-}$ and chromium(VI) species, such as CrO_4^{2-}. Radionuclides can be removed from radioactive and mixed waste by ion exchange resins.

22.6 PHOTOLYTIC REACTIONS

Photolytic (photochemical) **reactions** were discussed in Chapter 9 and as ideal "green chemistry" reagents in Chapter 20, Section 20.9. *Photolysis* can be used to destroy a number of kinds of hazardous wastes. In such applications it is most useful in breaking chemical bonds in refractory organic compounds. TCDD (see Section 7.10), one of the most troublesome and refractory of wastes, can be treated by ultraviolet radiation in the presence of hydrogen atom donors {H} resulting in reactions such as the following:



(22.6.1)

As photolysis proceeds, the H–C bonds are broken, the C–O bonds are broken, and the final product is a harmless organic polymer.

An initial photolysis reaction can result in the generation of reactive intermediates that participate in **chain reactions** that lead to the destruction of a

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compound. One of the most important reactive intermediates is free radical $HO^{\bullet}$. In some cases, **sensitizers** are added to the reaction mixture to absorb radiation and generate reactive species that destroy wastes.

Hazardous-waste substances other than TCDD that have been destroyed by photolysis are herbicides (atrazine), 2,4,6-trinitrotoluene (TNT), and polychlorinated biphenyls (PCBs). The addition of a chemical oxidant, such as potassium peroxydisulfate, $K_2S_2O_8$, enhances destruction by oxidizing active photolytic products.

22.7 THERMAL TREATMENT METHODS

Thermal treatment of hazardous wastes can be used to accomplish most of the common objectives of waste treatment—volume reduction; removal of volatile, combustible, mobile organic matter; and destruction of toxic and pathogenic materials. The most widely applied means of thermal treatment of hazardous wastes is **incineration**. Incineration utilizes high temperatures, an oxidizing atmosphere, and often turbulent combustion conditions to destroy wastes. Methods other than incineration that make use of high temperatures to destroy or neutralize hazardous wastes are discussed briefly at the end of this section.

Incineration

Hazardous-waste incineration will be defined here as a process that involves exposure of the waste materials to oxidizing conditions at a high temperature, usually in excess of 900˚C. Normally, the heat required for incineration comes from the oxidation of organically bound carbon and hydrogen contained in the waste material or in supplemental fuel:

$$C(\text{organic}) + O_2 \rightarrow CO_2 + \text{heat} \quad (22.7.1)$$

$$4H(\text{organic}) + O_2 \rightarrow 2H_2O + \text{heat} \quad (22.7.2)$$

These reactions destroy organic matter and generate heat required for endothermic reactions, such as the breaking of C–Cl bonds in organochlorine compounds.

Incinerable Wastes

Ideally, incinerable wastes are predominantly organic materials that will burn with a heating value of at least 5000 Btu/lb and preferably over 8000 Btu/lb. Such heating values are readily attained with wastes having high contents of the most commonly incinerated waste organic substances, including methanol, acetonitrile, toluene, ethanol, amyl acetate, acetone, xylene, methyl ethyl ketone, adipic acid, and ethyl acetate. In some cases, however, it is desirable to incinerate wastes that will not burn alone and that require **supplemental fuel,** such as methane and petroleum liquids. Examples of such wastes are nonflammable organochlorine wastes, some aqueous wastes, or soil in which the elimination of a particularly troublesome contaminant is worth the expense and trouble of incinerating it. Inorganic matter, water, and organic hetero element contents of liquid wastes are important in determining their incinerability.

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Hazardous-Waste Fuel

Many industrial wastes, including hazardous wastes, are burned as **hazardous-waste fuel** for energy recovery in industrial furnaces and boilers and in incinerators for nonhazardous wastes, such as sewage sludge incinerators. This process is called **coincineration**, and more combustible wastes are utilized by it than are burned solely for the purpose of waste destruction. In addition to heat recovery from combustible wastes, it is a major advantage to use an existing on-site facility for waste disposal rather than a separate hazardous-waste incinerator.

Incineration Systems

The four major components of hazardous-waste incineration systems are shown in Figure 22.8.

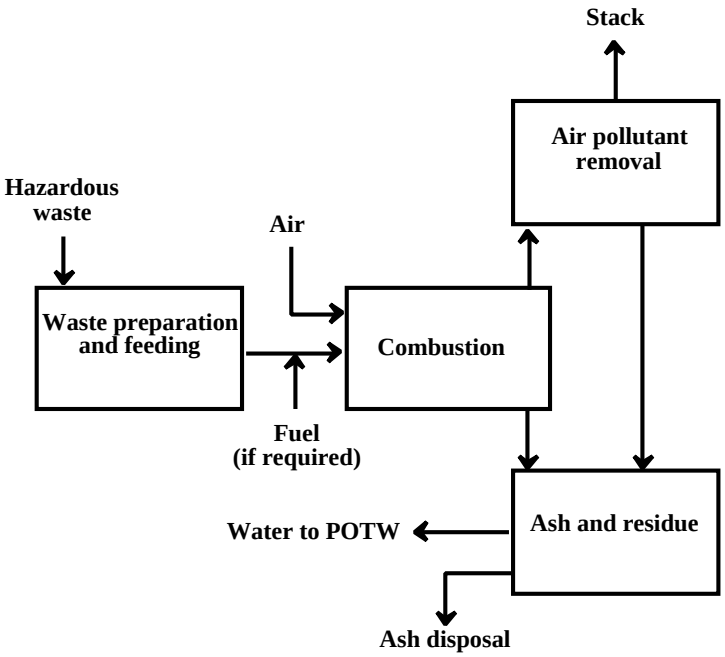


Figure 22.8 Major components of a hazardous-waste incinerator system.

Waste preparation for liquid wastes may require filtration, settling to remove solid material and water, blending to obtain the optimum incinerable mixture, or heating to decrease viscosity. Solids may require shredding and screening. Atomization is commonly used to feed liquid wastes. Several mechanical devices, such as rams and augers, are used to introduce solids into the incinerator.

The most common kinds of **combustion chambers** are liquid injection, fixed hearth, rotary kiln, and fluidized bed. These types are discussed in more detail later in this section.

Often the most complex part of a hazardous-waste incineration system is the **air pollution control system**, which involves several operations. The most common operations in air pollution control from hazardous-waste incinerators are combustion

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gas cooling, heat recovery, quenching, particulate matter removal, acid gas removal, and treatment and handling of by-product solids, sludges, and liquids.

Hot ash is often quenched in water. Prior to disposal it may require dewatering and chemical stabilization. A major consideration with hazardous-waste incinerators and the types of wastes that are incinerated is the disposal problem posed by the ash, especially with respect to potential leaching of heavy metals.

Types of Incinerators

hazardous-waste incinerators can be divided among the following, based upon type of combustion chamber:

- **Rotary kiln** (about 40% of U.S. hazardous-waste incinerator capacity) in which the primary combustion chamber is a rotating cylinder lined with refractory materials, and an afterburner downstream from the kiln to complete destruction of the wastes
- **Liquid injection** incinerators (also about 40% of U.S. hazardous-waste incinerator capacity) that burn pumpable liquid wastes dispersed as small droplets
- **Fixed-hearth incinerators** with single or multiple hearths upon which combustion of liquid or solid wastes occurs
- **Fluidized-bed incinerators** in which combustion of wastes is carried out on a bed of granular solid (such as limestone) maintained in a suspended (fluid-like) state by injection of air to remove pollutant acid gas and ash products
- **Advanced design incinerators** including **plasma incinerators** that make use of an extremely hot plasma of ionized air injected through an electrical arc;[12] **electric reactors** that use resistance-heated incinerator walls at around 2200˚C to heat and pyrolyze wastes by radiative heat transfer; **infrared systems**, which generate intense infrared radiation by passing electricity through silicon carbide resistance heating elements; **molten salt combustion** that uses a bed of molten sodium carbonate at about 900˚C to destroy the wastes and retain gaseous pollutants; and **molten glass processes** that use a pool of molten glass to transfer heat to the waste and to retain products in a poorly leachable glass form

Combustion Conditions

The key to effective incineration of hazardous wastes lies in the combustion conditions. These require (1) sufficient free oxygen in the combustion zone to ensure combustion of the wastes; (2) turbulence for thorough mixing of waste, oxidant, and (in cases where the waste does not have sufficient fuel content to be burned alone) supplemental fuel; (3) high combustion temperatures above about 900˚C to ensure that thermally resistant compounds do react; and (4) sufficient residence time (at least 2 seconds) to allow reactions to occur.

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Effectiveness of Incineration

EPA standards for hazardous-waste incineration are based upon the effectiveness of destruction of the **principal organic hazardous constituents** (POHC). Measurement of these compounds before and after incineration gives the **destruction removal efficiency** (DRE) according to the formula,

$$\text{DRE} = \frac{W_{in} - W_{out}}{W_{in}} \times 100 \qquad (22.7.3)$$

where W_{in} and W_{out} are the mass flow rates of the principal organic hazardous constituent (POHC) input and output (at the stack downstream from emission controls), respectively. United States EPA regulations call for destruction of 99.99% of POHCs and 99.9999% ("six nines") destruction of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, commonly called TCDD or "dioxin."

Wet Air Oxidation

Organic compounds and oxidizable inorganic species can be oxidized by oxygen in aqueous solution. The source of oxygen usually is air. Rather extreme conditions of temperature and pressure are required, with a temperature range of 175-327˚C and a pressure range of 300–3000 psig (2070–20700 kPa). The high pressures allow a high concentration of oxygen to be dissolved in the water, and the high temperatures enable the reaction to occur.

Wet air oxidation has been applied to the destruction of cyanides in electroplating wastewaters. The oxidation reaction for sodium cyanide is the following:

$$2Na^+ + 2CN^- + O_2 + 4H_2O \rightarrow 2Na^+ + 2HCO_3^- + 2NH_3 \qquad (22.7.4)$$

Organic wastes can be oxidized in supercritical water, taking advantage of the ability of supercritical fluids to dissolve organic compounds (see Section 22.4). Wastes are contacted with water and the mixture raised to a temperature and pressure required for supercritical conditions for water. Oxygen is then pumped in sufficient to oxidize the wastes. The process produces only small quantities of CO, and no SO_2 or NO_x. It can be used to degrade PCBs, dioxins, organochlorine insecticides, benzene, urea, and numerous other materials.

UV-Enhanced Wet Oxidation

Hydrogen peroxide (H_2O_2) can be used as an oxidant in solution assisted by ultraviolet radiation ($h\nu$). For the oxidation of organic species represented in general as $\{CH_2O\}$, the overall reaction is

$$2H_2O_2 + \{CH_2O\} + h\nu \rightarrow CO_2 + 3H_2O \qquad (22.7.5)$$

The ultraviolet radiation breaks chemical bonds and serves to form reactive oxidant species, such as $HO^{\bullet}$.

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22.8 BIODEGRADATION OF WASTES

Biodegradation of wastes is a term that describes the conversion of wastes by enzymatic biological processes to simple inorganic molecules (mineralization) and, to a certain extent, to biological materials. Usually the products of biodegradation are molecular forms that tend to occur in nature and that are in greater thermodynamic equilibrium with their surroundings than are the starting materials. **Detoxification** refers to the biological conversion of a toxic substance to a less toxic species. Microbial bacteria and fungi possessing enzyme systems required for biodegradation of wastes are usually best obtained from populations of indigenous microorganisms at a hazardous-waste site where the microorganisms have developed the ability to degrade particular kinds of molecules. Biological treatment offers a number of significant advantages and has considerable potential for the degradation of hazardous wastes, even *in situ*.

Under the label of **bioremediation**, the use of microbial processes to destroy hazardous wastes has been the subject of intense investigation in the waste-treatment community for a number of years. Doubts still exist about claims for its effectiveness in a number of applications. It must be kept in mind, however, that there are many factors that can cause biodegradation to fail as a treatment process. Often physical conditions are such that mixing of wastes, nutrients, and electron acceptor species (such as oxygen) is too slow to permit biodegradation to occur at a useful rate. Low temperatures may make reactions too slow to be useful. Toxicants, such as heavy metals, may inhibit biological activity, and some metabolites produced by the microorganisms may be toxic to them.

Biodegradability

The **biodegradability** of a compound is influenced by its physical characteristics, such as solubility in water and vapor pressure, and by its chemical properties, including molar mass, molecular structure, and presence of various kinds of functional groups, some of which provide a "biochemical handle" for the initiation of biodegradation. With the appropriate organisms and under the right conditions, even substances such as phenol that are considered to be biocidal to most microorganisms can undergo biodegradation.

Recalcitrant or **biorefractory** substances are those that resist biodegradation and tend to persist and accumulate in the environment. Such materials are not necessarily toxic to organisms, but simply resist their metabolic attack. However, even some compounds regarded as biorefractory can be degraded by microorganisms that have had the opportunity to adapt to their biodegradation; for example, DDT is degraded by properly acclimated *Pseudomonas*. Chemical pretreatment, especially by partial oxidation, can make some kinds of recalcitrant wastes much more biodegradable.

Properties of hazardous wastes and their media can be changed to increase biodegradability. This can be accomplished by adjustment of conditions to optimum temperature, pH (usually in the range of 6–9), stirring, oxygen level, and material load. Biodegradation can be aided by removal of toxic organic and inorganic substances, such as heavy–metal ions.

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Aerobic Treatment

Aerobic waste-treatment processes utilize aerobic bacteria and fungi that require molecular oxygen, O_2. These processes are often favored by microorganisms, in part because of the high energy yield obtained when molecular oxygen reacts with organic matter. Aerobic waste treatment is well adapted to the use of an activated sludge process. It can be applied to hazardous wastes such as chemical process wastes and landfill leachates. Some systems use powdered activated carbon as an additive to absorb organic wastes that are not biodegraded by microorganisms in the system.

Contaminated soils can be mixed with water and treated in a bioreactor to eliminate biodegradable contaminants in the soil. It is possible, in principle, to treat contaminated soils biologically in place by pumping oxygenated, nutrient-enriched water through the soil in a recirculating system.

Anaerobic Treatment

Anaerobic waste treatment in which microorganisms degrade wastes in the absence of oxygen can be practiced on a variety of organic hazardous wastes. Compared with the aerated activated sludge process, anaerobic digestion requires less energy; yields less sludge by-product; generates hydrogen sulfide (H_2S), which precipitates toxic heavy-metal ions; and produces methane gas, CH_4, which can be used as an energy source.

The overall process for anaerobic digestion is a fermentation process in which organic matter is both oxidized and reduced. The simplified reaction for the anaerobic fermentation of a hypothetical organic substance, "$\{CH_2O\}$", is the following:

$$2\{CH_2O\} \rightarrow CO_2 + CH_4 \qquad (22.8.1)$$

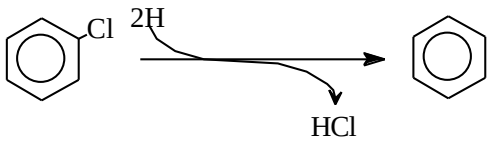
In practice, the microbial processes involved are quite complex. Most of the wastes for which anaerobic digestion is suitable consist of oxygenated compounds, such as acetaldehyde or methylethyl ketone.

Reductive Dehalogenation

Reductive dehalogenation is a mechanism by which halogen atoms are removed from organohalide compounds by anaerobic bacteria. It is an important means of detoxifying alkyl halides (particularly solvents), aryl halides, and organo-chlorine pesticides, all of which are important hazardous-waste compounds, and which were discarded in large quantities in some of the older waste disposal dumps. Reductive dehlogenation is the only means by which some of the more highly halogenated waste compounds are biodegraded; such compounds include tetra-chloroethene, hexachlorobenzene, pentachlorophenol, and the more highly chlorinated PCB congeners.[13]

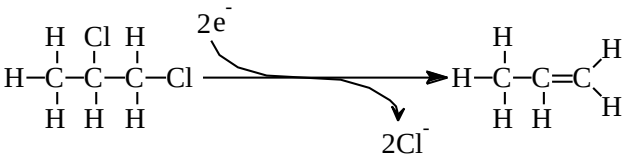
The two general processes by which reductive dehalogenation occurs are **hydrogenolysis**, as shown by the example in Equation 22.8.2,

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(22.8.2)

and **vicinal reduction**



(22.8.3)

Vicinal reduction removes two adjacent halogen atoms, and works only on alkyl halides, not aryl halides. Both processes produce innocuous inorganic halide (Cl^-).

22.9 LAND TREATMENT AND COMPOSTING

Land Treatment

Soil can be viewed as a natural filter for wastes. Soil has physical, chemical, and biological characteristics that can enable waste detoxification, biodegradation, chemical decomposition, and physical and chemical fixation. Therefore, **land treatment** of wastes can be accomplished by mixing the wastes with soil under appropriate conditions.

Soil is a natural medium for a number of living organisms that may have an effect upon biodegradation of hazardous wastes. Of these, the most important are bacteria, including those from the genera *Agrobacterium*, *Arthrobacteri*, *Bacillus*, *Flavobacterium,* and *Pseudomonas. Actinomycetes* and fungi are important organisms in decay of vegetable matter and may be involved in biodegradation of wastes.

Microorganisms useful for land treatment of wastes are usually present naturally in sufficient numbers to provide the inoculum required for their growth. The growth of these indigenous microorganisms can be stimulated by adding nutrients and an electron acceptor to act as an oxidant (for aerobic degradation) accompanied by mixing. The most commonly added nutrients are nitrogen and phosphorus. Oxygen can be added by pumping air underground or by treatment with hydrogen peroxide, H_2O_2. In some cases, such as for treatment of hydrocarbons on or near the soil surface, simple tillage provides both oxygen and the mixing required for optimum microbial growth.

Wastes that are amenable to land treatment are biodegradable organic substances. However, in soil contaminated with hazardous wastes, bacterial cultures may develop that are effective in degrading normally recalcitrant compounds through acclimation over a long period of time. Land treatment is most used for petroleum refining wastes and is applicable to the treatment of fuels and wastes from leaking underground storage tanks. It can also be applied to biodegradable organic chemical wastes, including some organohalide compounds. Land treatment is not

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suitable for the treatment of wastes containing acids, bases, toxic inorganic compounds, salts, heavy metals, and organic compounds that are excessively soluble, volatile, or flammable.

Composting

Composting of hazardous wastes is the biodegradation of solid or solidified materials in a medium other than soil. Bulking material, such as plant residue, paper, municipal refuse, or sawdust can be added to retain water and enable air to penetrate to the waste material. Successful composting of hazardous waste depends upon a number of factors, including those discussed above under land treatment. The first of these is the selection of the appropriate microorganism or **inoculum**. Once a successful composting operation is underway, a good inoculum is maintained by recirculating spent compost to each new batch. Other parameters that must be controlled include oxygen supply, moisture content (which should be maintained at a minimum of about 40%), pH (usually around neutral), and temperature. The composting process generates heat, so, if the mass of the compost pile is sufficiently high, it can be self-heating under most conditions. Some wastes are deficient in nutrients such as nitrogen, which must be supplied from commercial sources or from other wastes.

22.10 PREPARATION OF WASTES FOR DISPOSAL

Immobilization, stabilization, fixation, and solidification are terms that describe sometimes overlapping techniques whereby hazardous wastes are placed in a form suitable for long-term disposal. These aspects of hazardous-waste management are addressed below.

Immobilization

Immobilization includes physical and chemical processes that reduce surface areas of wastes to minimize leaching. It isolates the wastes from their environment, especially groundwater, so that they have the least possible tendency to migrate. This is accomplished by physically isolating the waste, reducing its solubility, and decreasing its surface area. Immobilization usually improves the handling and physical characteristics of wastes.

Stabilization

Stabilization means the conversion of a waste from its original form to a physically and chemically more stable material that is less likely to cause problems during handling and disposal, and less likely to be mobile after disposal. Stabilization can include chemical reactions that generate products that are less volatile, soluble, and reactive. Solidification, which is discussed below, is one of the most common means of stabilization. Stabilization is required for land disposal of wastes. **Fixation** is a process that binds a hazardous waste in a less mobile and less toxic form; it means much the same thing as stabilization.

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Solidification

Solidification may involve chemical reaction of the waste with the solidification agent, mechanical isolation in a protective binding matrix, or a combination of chemical and physical processes. It can be accomplished by evaporation of water from aqueous wastes or sludges, sorption onto solid material, reaction with cement, reaction with silicates, encapsulation, or embedding in polymers or thermoplastic materials.

In many solidification processes, such as reaction with Portland cement, water is an important ingredient of the hydrated solid matrix. Therefore, the solid should not be heated excessively or exposed to extremely dry conditions, which could result in diminished structural integrity from loss of water. In some cases, however, heating a solidified waste is an essential part of the overall solidification procedure. For example, an iron hydroxide matrix can be converted to highly insoluble, refractory iron oxide by heating. Organic constituents of solidified wastes can be converted to inert carbon by heating. Heating is an integral part of the process of vitrification (see below).

Sorption to a Solid Matrix Material

Hazardous-waste liquids, emulsions, sludges, and free liquids in contact with sludges can be solidified and stabilized by fixing onto solid **sorbents**, including activated carbon (for organics), fly ash, kiln dust, clays, vermiculite, and various proprietary materials. Sorption can be done to convert liquids and semisolids to dry solids, improve waste handling, and reduce solubility of waste constituents. Sorption can also be used to improve waste compatibility with substances such as Portland cement used for solidification and setting. Specific sorbents can also be used to stabilize pH and pE (a measure of the tendency of a medium to be oxidizing or reducing, see Chapter 4).

The action of sorbents can include simple mechanical retention of wastes, physical sorption, and chemical reactions. It is important to match the sorbent to the waste. A substance with a strong affinity for water should be employed for wastes containing excess water, and one with a strong affinity for organic materials should be used for wastes with excess organic solvents.

Thermoplastics and Organic Polymers

Thermoplastics are solids or semisolids that become liquified at elevated temperatures. Hazardous-waste materials can be mixed with hot thermoplastic liquids and solidified in the cooled thermoplastic matrix, which is rigid but deformable. The thermoplastic material most used for this purpose is asphalt bitumen. Other thermoplastics, such as paraffin and polyethylene, have also been used to immobilize hazardous wastes.

Among the wastes that can be immobilized with thermoplastics are those containing heavy metals, such as electroplating wastes. Organic thermoplastics repel water and reduce the tendency toward leaching in contact with groundwater. Compared with cement, thermoplastics add relatively less material to the waste.

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A technique similar to that described above uses **organic polymers** produced in contact with solid wastes to embed the wastes in a polymer matrix. Three kinds of polymers that have been used for this purpose include polybutadiene, urea-formaldehyde, and vinyl ester-styrene polymers. This procedure is more complicated than is the use of thermoplastics but, in favorable cases, yields a product in which the waste is held more strongly.

Vitrification

Vitrification, or **glassification**, consists of embedding wastes in a glass material. In this application, glass can be regarded as a high-melting-temperature inorganic thermoplastic. Molten glass can be used, or glass can be synthesized in contact with the waste by mixing and heating with glass constituents—silicon dioxide (SiO_2), sodium carbonate (Na_2CO_3), and calcium oxide (CaO). Other constituents may include boron oxide, B_2O_3, which yields a borosilicate glass that is especially resistant to changes in temperature and chemical attack. In some cases, glass is used in conjunction with thermal waste destruction processes, serving to immobilize hazardous-waste ash consituents. Some wastes are detrimental to the quality of the glass. Aluminum oxide, for example, may prevent glass from fusing.

Vitrification is relatively complicated and expensive, the latter because of the energy consumed in fusing glass. Despite these disadvantages, it is the favored immobilization technique for some special wastes and has been promoted for solidification of radionuclear wastes because glass is chemically inert and resistant to leaching. However, high levels of radioactivity can cause deterioration of glass and lower its resistance to leaching.

Solidification with Cement

Portland cement is widely used for solidification of hazardous wastes. In this application, Portland cement provides a solid matrix for isolation of the wastes, chemically binds water from sludge wastes, and may react chemically with wastes (for example, the calcium and base in Portland cement react chemically with inorganic arsenic sulfide wastes to reduce their solubilities). However, most wastes are held physically in the rigid Portland cement matrix and are subject to leaching.

As a solidification matrix, Portland cement is most applicable to inorganic sludges containing heavy metal ions that form insoluble hydroxides and carbonates in the basic carbonate medium provided by the cement. The success of solidification with Portland cement strongly depends upon whether the waste adversely affects the strength and stability of the concrete product. A number of substances—organic matter such as petroleum or coal; some silts and clays; sodium salts of arsenate, borate, phosphate, iodate, and sulfide; and salts of copper, lead, magnesium, tin, and zinc—are incompatible with Portland cement because they interfere with its set and cure, producing a mechanically weak product and resulting in deterioration of the cement matrix with time. However, a reasonably good disposal form can be obtained by absorbing organic wastes with a solid material, which in turn is set in Portland cement.

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Solidification with Silicate Materials

Water-insoluble **silicates**, (pozzolanic substances) containing oxyanionic silicon such as SiO_3^{2-} are used for waste solidification. There are a number of such substances, some of which are waste products, including fly ash, flue dust, clay, calcium silicates, and ground-up slag from blast furnaces. Soluble silicates, such as sodium silicate, may also be used. Silicate solidification usually requires a setting agent, which may be Portland cement (see above), gypsum (hydrated $CaSO_4$), lime, or compounds of aluminum, magnesium, or iron. The product can vary from a granular material to a concrete-like solid. In some cases, the product is improved by additives, such as emulsifiers, surfactants, activators, calcium chloride, clays, carbon, zeolites, and various proprietary materials.

Success has been reported for the solidification of both inorganic wastes and organic wastes (including oily sludges) with silicates. The advantages and disadvantages of silicate solidification are similar to those of Portland cement discussed above. One consideration that is especially applicable to fly ash is the presence in some silicate materials of leachable hazardous substances, which may include arsenic and selenium.

Encapsulation

As the name implies, **encapsulation** is used to coat wastes with an impervious material so that they do not contact their surroundings. For example, a water-soluble waste salt encapsulated in asphalt would not dissolve so long as the asphalt layer remains intact. A common means of encapsulation uses heated, molten thermoplastics, asphalt, and waxes that solidify when cooled. A more sophisticated approach to encapsulation is to form polymeric resins from monomeric substances in the presence of the waste.

Chemical Fixation

Chemical fixation is a process that binds a hazardous-waste substance in a less mobile, less toxic form by a chemical reaction that alters the waste chemically. Physical and chemical fixation often occur together, and sometimes it is a little difficult to distinguish between them. Polymeric inorganic silicates containing some calcium and often some aluminum are the inorganic materials most widely used as a fixation matrix. Many kinds of heavy metals are chemically bound in such a matrix, as well as being held physically by it. Similarly, some organic wastes are bound by reactions with matrix constituents.

22.11 ULTIMATE DISPOSAL OF WASTES

Regardless of the destruction, treatment, and immobilization techniques used, there will always remain from hazardous wastes some material that has to be put somewhere. This section briefly addresses the ultimate disposal of ash, salts, liquids, solidified liquids, and other residues that must be placed where their potential to do harm is minimized.

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Disposal Above Ground

In some important respects disposal above ground, essentially in a pile designed to prevent erosion and water infiltration, is the best way to store solid wastes. Perhaps its most important advantage is that it avoids infiltration by groundwater that can result in leaching and groundwater contamination common to storage in pits and landfills. In a properly designed above-ground disposal facility, any leachate that is produced drains quickly by gravity to the leachate collection system, where it can be detected and treated.

Aboveground disposal can be accomplished with a storage mound deposited on a layer of compacted clay covered with impermeable membrane liners laid somewhat above the original soil surface and shaped to allow leachate flow and collection. The slopes around the edges of the storage mound should be sufficiently great to allow good drainage of precipitation, but gentle enough to deter erosion.

Landfill

Landfill historically has been the most common way of disposing of solid hazardous wastes and some liquids, although it is being severely limited in many nations by new regulations and high land costs. Landfill involves disposal that is at least partially underground in excavated cells, quarries, or natural depressions. Usually fill is continued above ground to utilize space most efficiently and provide a grade for drainage of precipitation.

The greatest environmental concern with landfill of hazardous wastes is the generation of leachate from infiltrating surface water and groundwater with resultant contamination of groundwater supplies. Modern hazardous-waste landfills provide elaborate systems to contain, collect, and control such leachate.

There are several components to a modern landfill. A landfill should be placed on a compacted, low-permeability medium, preferably clay, which is covered by a flexible-membrane liner consisting of watertight impermeable material. This liner is covered with granular material in which is installed a secondary drainage system. Next is another flexible-membrane liner, above which is installed a primary drainage system for the removal of leachate. This drainage system is covered with a layer of granular filter medium, upon which the wastes are placed. In the landfill, wastes of different kinds are separated by berms consisting of clay or soil covered with liner material. When the fill is complete, the waste is capped to prevent surface water infiltration and covered with compacted soil. In addition to leachate collection, provision may be made for a system to treat evolved gases, particularly when methane-generating biodegradable materials are disposed in the landfill.

The flexible-membrane liner made of rubber (including chlorosulfonated polyethylene) or plastic (including chlorinated polyethylene, high-density polyethylene, and polyvinylchloride) is a key component of state-of-the-art landfills. It controls seepage out of, and infiltration into, the landfill. Obviously, liners must meet stringent standards to serve their intended purpose. In addition to being impermeable, the liner material must be strongly resistant to biodegradation, chemical attack, and tearing.

Capping is done to cover the wastes, prevent infiltration of excessive amounts of surface water, and prevent release of wastes to overlying soil and the atmosphere.

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Caps come in a variety of forms and are often multilayered. Some of the problems that may occur with caps are settling, erosion, ponding, damage by rodents, and penetration by plant roots.

Surface Impoundment of Liquids

Many liquid hazardous wastes, slurries, and sludges are placed in **surface impoundments**, which usually serve for treatment and often are designed to be filled in eventually as landfill disposal sites. Most liquid hazardous wastes and a significant fraction of solids are placed in surface impoundments in some stage of treatment, storage, or disposal.

A surface impoundment may consist of an excavated "pit," a structure formed with dikes, or a combination thereof. The construction is similar to that discussed above for landfills in that the bottom and walls should be impermeable to liquids and provision must be made for leachate collection. The chemical and mechanical challenges to liner materials in surface impoundments are severe so that proper geological siting and construction with floors and walls composed of low-permeability soil and clay are important in preventing pollution from these installations.

Deep-Well Disposal of Liquids

Deep-well disposal of liquids consists of their injection under pressure to underground strata isolated by impermeable rock strata from aquifers. Early experience with this method was gained in the petroleum industry where disposal is required of large quantities of saline wastewater coproduced with crude oil. The method was later extended to the chemical industry for the disposal of brines, acids, heavy metal solutions, organic liquids, and other liquids.

A number of factors must be considered in deep-well disposal. Wastes are injected into a region of elevated temperature and pressure, which may cause chemical reactions to occur involving the waste constituents and the mineral strata. Oils, solids, and gases in the liquid wastes can cause problems such as clogging. Corrosion may be severe. Microorganisms may have some effects. Most problems from these causes can be mitigated by proper waste pretreatment.

The most serious consideration involving deep-well disposal is the potential contamination of groundwater. Although injection is made into permeable saltwater aquifers presumably isolated from aquifers that contain potable water, contamination may occur. Major routes of contamination include fractures, faults, and other wells. The disposal well itself can act as a route for contamination if it is not properly constructed and cased or if it is damaged.

22.12 LEACHATE AND GAS EMISSIONS

Leachate

The production of contaminated leachate is a possibility with most disposal sites. Therefore, new hazardous-waste landfills require leachate collection/treatment systems and many older sites are required to have such systems retrofitted to them.

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Modern hazardous-waste landfills typically have dual leachate collection systems, one located between the two impermeable liners required for the bottom and sides of the landfill, and another just above the top liner of the double-liner system. The upper leachate collection system is called the primary leachate collection system, and the bottom is called the secondary leachate collection system. Leachate is collected in perforated pipes that are embedded in granular drain material.

Chemical and biochemical processes have the potential to cause some problems for leachate collection systems. One such problem is clogging by insoluble manganese(IV) and iron(III) hydrated oxides upon exposure to air as described for water wells in Section 15.9.

Leachate consists of water that has become contaminated by wastes as it passes through a waste-disposal site. It contains waste constituents that are soluble, not retained by soil, and not degraded chemically or biochemically. Some potentially harmful leachate constituents are products of chemical or biochemical transformations of wastes.

The best approach to leachate management is to prevent its production by limiting infiltration of water into the site. Rates of leachate production may be very low when sites are selected, designed, and constructed with minimal production of leachate as a major objective. A well-maintained, low-permeability cap over the landfill is very important for leachate minimization.

Hazardous-Waste Leachate Treatment

The first step in treating leachate is to characterize it fully, particularly with a thorough chemical analysis of possible waste constituents and their chemical and metabolic products. The biodegradability of leachate constituents should also be determined.

The options available for the treatment of hazardous-waste leachate are generally those that can be used for industrial wastewaters. These include biological treatment by an activated sludge or related process, and sorption by activated carbon, usually in columns of granular activated carbon. Hazardous-waste leachate can be treated by a variety of chemical processes, including acid-base neutralization, precipitation, and oxidation-reduction. In some cases, these treatment steps must precede biological treatment; for example, leachate exhibiting extremes of pH must be neutralized for microorganisms to thrive in it. Cyanide in the leachate can be oxidized with chlorine and organics with ozone, hydrogen peroxide promoted with ultraviolet radiation, or dissolved oxygen at high temperatures and pressures. Heavy metals can be precipitated with base, carbonate, or sulfide.

Leachate can be treated by a variety of physical processes. In some cases, simple density separation and sedimentation can be used to remove water-immiscible liquids and solids. Filtration is frequently required and flotation can be useful. Leachate solutes can be concentrated by evaporation, distillation, and membrane processes, including reverse osmosis, hyperfiltration, and ultrafiltration. Organic constituents can be removed from leachate by solvent extraction, air stripping, or steam stripping. In the case of volatile organic compounds in leachate (VOCs), care must be exercised to prevent excessive escape to the atmosphere, thus creating an air pollution problem as the result of leachate treatment.

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Gas Emissions

In the presence of biodegradable wastes, methane and carbon dioxide gases are produced in landfills by anaerobic degradation (see Reaction 22.8.1). Gases can also be produced by chemical processes with improperly pretreated wastes, as would occur in the hydrolysis of calcium carbide to produce acetylene:

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2 \qquad (22.12.1)$$

Odorous and toxic hydrogen sulfide, H_2S, can be generated by the chemical reaction of sulfides with acids or by the biochemical reduction of sulfate by anaerobic bacteria (*Desulfovibrio*) in the presence of biodegradable organic matter:

$$SO_4^{2-} + 2\{CH_2O\} + 2H^+ \xrightarrow[\text{bacteria}]{\text{Anaerobic}} H_2S + 2CO_2 + 2H_2O \qquad (22.12.2)$$

Gases such as these may be toxic, combustible, or explosive. Furthermore, gases permeating through landfilled hazardous waste may carry along waste vapors, such as those of volatile aryl compounds and low-molar-mass halogenated hydrocarbons. Of these, the ones of most concern are benzene, 1,2-dibromoethane, 1,2-dichloroethane, carbon tetrachloride, chloroform, dichloromethane, tetrachloroethane, 1,1,1-trichloroethane, trichloroethylene, and vinyl chloride. Because of the hazards from these and other volatile species, it is important to minimize production of gases and, if significant amounts of gases are produced, they should be vented or treated by activated carbon sorption or flaring.

22.13 *IN-SITU* TREATMENT

***In-situ* treatment** refers to waste treatment processes that can be applied to wastes in a disposal site by direct application of treatment processes and reagents to the wastes. Where possible, *in-situ* treatment is desirable for waste site remediation.

In-Situ Immobilization

In-situ immobilization is used to convert wastes to insoluble forms that will not leach from the disposal site. Heavy metal contaminants including lead, cadmium, zinc, and mercury, can be immobilized by chemical precipitation as the sulfides by treatment with gaseous H_2S or alkaline Na_2S solution. Disadvantages include the high toxicity of H_2S and the contamination potential of soluble sulfide. Although precipitated metal sulfides should remain as solids in the anaerobic conditions of a landfill, unintentional exposure to air can result in oxidation of the sulfide and remobilization of the metals as soluble sulfate salts.

Oxidation and reduction reactions can be used to immobilize heavy metals *in-situ*. Oxidation of soluble Fe^{2+} and Mn^{2+} to their insoluble hydrous oxides, $Fe_2O_3 \cdot xH_2O$ and $MnO_2 \cdot xH_2O$, respectively, can precipitate these metal ions and coprecipitate other heavy-metal ions. However, subsurface reducing conditions could later result in reformation of soluble reduced species. Reduction can be used *in situ* to convert soluble, toxic chromate to insoluble chromium(III) compounds.

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Chelation can convert metal ions to less mobile forms, although with most agents, chelation has the opposite effect. A chelating agent called Tetran is supposed to form metal chelates that are strongly bound to clay minerals. The humin fraction of soil humic substances likewise immobilizes metal ions.

Vapor Extraction

Many important wastes have relatively high vapor pressures and can be removed by vapor extraction. This technique works for wastes in soil above the level of groundwater, that is, in the vadose zone. Simple in concept, vapor extraction involves pumping air into injection wells in soil and withdrawing it, along with volatile components that it has picked up, through extraction wells. The substances vaporized from the soil are removed by activated carbon or by other means. In some cases, the air is pumped through an engine (which can be used to run the air pumps) and are destroyed by conditions in the engine's combustion chambers. It is relatively efficient compared with groundwater pumping because of the much higher flow rates of air through soil compared with water. Vapor extraction is most applicable to the removal of volatile organic compounds (VOCs) such as chloromethanes, chloroethanes, chloroethylenes (such as trichloroethylene), benzene, toluene, and xylene.

Solidification InSitu

In-situ solidification can be used as a remedial measure at hazardous-waste sites. One approach is to inject soluble silicates followed by reagents that cause them to solidify. For example, injection of soluble sodium silicate followed by calcium chloride or lime forms solid calcium silicate.

Detoxification *In Situ*

When only one or a limited number of harmful constituents is present in a waste-disposal site, it may be practical to consider detoxification *in-situ*. This approach is most practical for organic contaminants including pesticides (organophosphate esters and carbamates), amides, and esters. Among the chemical and biochemical processes that can detoxify such materials are chemical and enzymatic oxidation, reduction, and hydrolysis. Chemical oxidants that have been proposed for this purpose include hydrogen peroxide, ozone, and hypochlorite.

Enzyme extracts collected from microbial cultures and purified have been considered for *in-situ* detoxification. One cell-free enzyme that has been used for detoxification of organophosphate insecticides is parathion hydrolase. The hostile environment of a chemical-waste landfill, including the presence of enzyme-inhibiting heavy-metal ions, is detrimental to many biochemical approaches to *in-situ* treatment. Furthermore, most sites contain a mixture of hazardous constituents, which might require several different enzymes for their detoxification.

Permeable-Bed Treatment

Some groundwater plumes contaminated by dissolved wastes can be treated by a permeable bed of material placed in a trench through which the groundwater must

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flow. Limestone in a permeable bed neutralizes acid and precipitates some heavy metal hydroxides or carbonates. Synthetic ion exchange resins can be used in a permeable bed to retain heavy metals and even some anionic species, although competition with ionic species present naturally in the groundwater can cause some problems with their use. Activated carbon in a permeable bed will remove some organics, especially less soluble, higher molar mass organic compounds.

Permeable-bed treatment requires relatively large quantities of reagent, which argues against the use of activated carbon and ion exchange resins. In such an application it is unlikely that either of these materials could be reclaimed and regenerated as is done when they are used in columns to treat wastewater. Furthermore, ions taken up by ion exchangers and organic species retained by activated carbon may be released at a later time, causing subsequent problems. Finally, a permeable bed that has been truly effective in collecting waste materials may, itself, be considered a hazardous waste requiring special treatment and disposal.

In-Situ Thermal Processes

Heating of wastes *in situ* can be used to remove or destroy some kinds of hazardous substances. Steam injection and radio frequency and microwave heating have been proposed for this purpose. Volatile wastes brought to the surface by heating can be collected and held as condensed liquids or by activated carbon.

One approach to immobilizing wastes *in-situ* is high temperature vitrification using electrical heating. This process involves pouring conducting graphite on the surface between two electrodes and passing an electric current between the electrodes. In principle, the graphite becomes very hot and "melts" into the soil, leaving a glassy slag in its path. Volatile species evolved are collected and, if the operation is successful, a nonleachable slag is left in place. It is easy to imagine problems that might occur, including difficulties in getting a uniform melt, problems from groundwater infiltration, and very high consumption of electricity.

Soil Washing and Flushing

Extraction with water containing various additives can be used to cleanse soil contaminated with hazardous wastes. When the soil is left in place and the water pumped into and out of it, the process is called **flushing**; when soil is removed and contacted with liquid the process is referred to as **washing**. Here, washing is used as a term applied to both processes.

The composition of the fluid used for soil washing depends upon the contaminants to be removed. The washing medium may consist of pure water or it may contain acids (to leach out metals or neutralize alkaline soil contaminants), bases (to neutralize contaminant acids), chelating agents (to solubilize heavy metals), surfactants (to enhance the removal of organic contaminants from soil and improve the ability of the water to emulsify insoluble organic species), or reducing agents (to reduce oxidized species). Soil contaminants may dissolve, form emulsions, or react chemically. Heavy metal salts; lighter aromatic hydrocarbons, such as toluene and xylenes; lighter organohalides, such as trichloro- or tetrachloroethylene; and light-to-medium molar mass aldehydes and ketones can be removed from soil by washing.

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CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

In descending order of desirability, the five objectives of hazardous-waste management are [1]_____

_____.
The **effectiveness** of a hazardous-waste management system is a measure of [2]_____
_____.
By its nature, a system of industrial ecology is also a system of waste _____
_____. Cutting down quantities of wastes from their sources is known as [3]_____ and utilization of treatment processes that reduce the quantities of wastes requiring ultimate disposal is called [4]_____. The most effective approach to minimizing wastes is to emphasize [5]_____
_____. A crucial part of the process for reducing and minimizing wastes is the development of a [6]_____ balance.
The four broad areas in which something of value can be obtained from recycling wastes are [7]_____

_____.
Some of the more important examples of substances recycled are [8]_____

_____.
Annual production of potentially recyclable waste oil in the United States is approximately [9]_____, of which around half is [10]_____
_____. Waste oil that is to be used for fuel is given [11]_____
treatment of a [12]_____ nature. The most important operation in solvent purification and recycling is [13]_____. Two of the major potential pollution problems with industrial water recycling are [14]_____
_____. Although wastewater distillation, treatment with activated carbon, reverse osmosis, and other treatment processes produce very high quality water for recycling they have the disadvantage of [15]_____
_____. Waste treatment can occur at the three major levels of [16]_____
_____. Major categories of physical waste treatment include [17]_____
_____. Means of separation of components of a waste mixture that are already in two different phases include [18]_____

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_____.
Physical separation by phase transition is best exemplifed by [19]_____, a potential waste problem resulting from which is production of [20]_____ _____. Common means of removing solvent from a waste, other than distillation are [21]_____ _____. Separating volatile components from less volatile ones in a liquid mixture by the partitioning of the more volatile materials to a gas phase of air or steam is called [22]_____. Physical precipitation describes [23]_____ _____. An important example of phase transfer involving two liquids and at least one solute is [24]_____ _____. The most common supercritical fluid used for extraction is [25]_____. Transfer of a substance from a solution to a solid phase is called [26]_____ and the most common sorbent, especially for organic compounds, is [27]_____. Molecular separation is often based upon [28]_____, of which the most widely used is [29]_____ _____. The chemical properties of constituents of a waste that generally determine the kind of chemical treatment to which it may be subjected are [30]_____ _____ _____.
Common unit operations in chemical treatment of wastes are [31]_____ _____ _____. Waste acids and bases are treated by [32]_____. Chemical precipitation is used in hazardous-waste treatment primarily for the removal of [33]_____ from water. Some metals can be precipitated from solution in the elemental metal form by the action of [34]_____ _____. Displacement from solution into the elemental state of a dissolved hazardous metal through the action of a nonhazardous elemental metal is a treatment process called [35]_____. A strong oxidant that can be generated on-site by an electrical discharge through dry air or oxygen then used for waste treatment is [36]_____. Electrolysis is a waste-treatment process in which [37]_____ _____ _____.
A chemical waste treatment process that could be used to treat metal hydrides, alkoxides, nonmetal oxyhalides, and organic anhydrides is [38]_____ _____. Reducing agents might be used to treat soils to remove [39]_____ _____. Cations or anions are removed from solution onto a solid resin, which can be regenerated by treatment with acids, bases, or salts through a process called [40]_____. In waste treatment, photochemical reactions are used for [41]_____ _____. In some cases where photochemical means are used for waste treatment, sensitizers are added to the reaction mixture to [42]_____

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_____. A process that utilizes high temperatures, an oxidizing atmosphere, and often turbulent combustion conditions to destroy wastes is [43]_____. The two most widely used types of hazardous-waste incinerators are [44]_____. Effectiveness of incineration is measured by destruction of the [45]_____ _____ and expressed as [46]_____ _____. United States EPA regulations call for destruction/removal of [47]_____ percent of POHCs and [48]_____ percent of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. Wet air oxidation involves [49]_____ _____, a process that can be enhanced by [50]_____. The use of microbial processes to destroy hazardous wastes is called [51]_____. Hazardous-waste substances that resist biodegradation are termed [52]_____ _____. Aerobic waste treatment utilizes bacteria and or fungi that require [53]_____. The overall process for anaerobic digestion of wastes is a [54]_____ process in which organic matter is both [55]_____. Reductive dehalogenation is a mechanism by which [56]_____ are removed from organohalide compounds by the action of [57]_____. Land treatment of wastes may be accomplished by [58]_____ _____. Composting of hazardous wastes is the biodegradation of solid or solidified materials [59]_____ _____. Immobilization of wastes includes physical and chemical processes that [60]_____ _____. Stabilization means conversion of waste to a form that is less likely to be [61]_____ after disposal. For solidifying and stabilizing organic wastes a good solid sorbent to use is [62]_____. For disposal, hazardous-waste materials can be mixed with hot [63]_____ liquids and solidified in the cooled [64]_____ _____ matrix, which is rigid but deformable. Vitrification consists of imbedding wastes in a [65]_____ material. A common construction material used to solidify hazardous wastes for disposal is [66]_____. Pozzolanic substances used for waste disposal consist of [67]_____ _____. Chemical fixation is a process that binds a hazardous-waste substance in a less mobile, less toxic form by [68]_____ _____. Historically, [69]_____ has been the most common way of disposing of solid hazardous wastes and some liquids. The greatest potential problem with this means of waste disposal is [70]_____ _____. Injection of wastes into underground strata isolated by impermeable rock strata from aquifers is referred to as [71]_____. The most common water pollution problem arising from waste disposal is [72]_____ and the most common air pollution problem is [73]_____. Treating wastes in place in the ground is referred to as [74]_____. Excavation down to a plume of waste flow underground and placing a substance for treatment in the path of the plume is known as [75]_____. Treating contaminated soil left in place by pumping water into and out of it is a

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process called [76]_____; when soil is removed and contacted with liquid the process is referred to as [77]_____.

Answers to Chapter Summary

1. (1) do not produce it, (2) if making it cannot be avoided, produce only minimum quantities, (3) recycle it, (3) if it is produced and cannot be recycled, treat it, preferably in a way that makes it nonhazardous, (4) if it cannot be rendered nonhazardous, dispose of it in a safe manner, (5) once it is disposed of, monitor it for leaching and other adverse effects
2. how well it reduces the quantities and hazards of wastes
3. waste reduction
4. waste minimization
5. waste minimization as an integral part of plant design
6. material
7. (1) direct recycle as raw material to the generator, as with the return to feedstock of raw materials not completely consumed in a synthesis process, (2) transfer as a raw material to another process; a substance that is a waste product from one process may serve as a raw material for another, sometimes in an entirely different industry, (3) utilization for pollution control or waste treatment, such as use of waste alkali to neutralize waste acid, (4) recovery of energy, for example, from the incineration of combustible hazardous wastes.
8. ferrous metals, nonferrous metals, metal compounds, inorganic substances, glass, paper, plastic, rubber, organic substances, catalysts, and materials with agricultural uses
9. 4 billion liters
10. burned as fuel
11. minimal
12. physical
13. fractional distillation
14. heavy metals and dissolved toxic organic species
15. producing potentially hazardous byproducts
16. primary, secondary, and polishing
17. phase separation, phase transfer, phase transition, and membrane separations
18. sedimentation and decanting, filtration, centrifugation, flotation
19. distillation
20. distillation bottoms
21. evaporation, including thin-film evaporation, and drying, including freeze drying
22. stripping
23. processes in which a solid forms from a solute in solution as a result of a physical change in the solution
24. solvent extraction
25. carbon dioxide
26. sorption
27. activated carbon
28. membrane processes
29. reverse osmosis

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30. acid-base, oxidation-reduction, precipitation, and complexation behavior; reactivity; flammability/combustibility; corrosivity; and compatibility with other wastes
31. acid-base neutralization, chemical precipitation, chemical extraction and leaching, oxidation, reduction, and ion exchange
32. neutralization
33. heavy-metal ions
34. a reducing agent such as sodium borohydride
35. cementation
36. ozone
37. one species in solution (usually a metal ion) is reduced by electrons at the cathode and another gives up electrons to the anode and is oxidized there
38. hydrolysis, the reaction with water
39. heavy metals coprecipitated with Fe_2O_3or MnO_2
40. ion exchange
41. breaking chemical bonds in refractory organic compounds
42. absorb radiation and generate reactive species that destroy wastes
43. incineration
44. rotary kiln and liquid injection
45. principal organic hazardous constituents
46. destruction removal efficiency
47. 99.99
48. 99.9999
49. oxidizing wastes in water at high temperatures and very high pressures
50. ultraviolet radiation
52. refractory or recalcitrant
53. molecular oxygen
54. fermentation
55. oxidized and reduced
56. halogen atoms
57. anaerobic bacteria
58. mixing the wastes with soil under appropriate conditions
59. in a medium other than soil
60. reduce surface areas of wastes to minimize leaching
61. mobile
62. activated carbon
63. thermoplastic
64. thermoplastic
65. glass
66. Portland cement
67. water-insoluble silicates
68. a chemical reaction that alters the waste chemically
69. landfill
70. production of leachate that may contaminate groundwater
71. deep well disposal
72. production of leachate
73. release of gases
74. *in-situ* treatment

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75. permeable-bed treatment
76. soil flushing
77. soil washing

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QUESTIONS AND PROBLEMS

1. Place the following in descending order of desirability for dealing with wastes and discuss your rationale for doing so: (a) reducing the volume of remaining wastes by measures such as incineration, (b) placing the residual material in landfills, properly protected from leaching or release by other pathways, (c) treating residual material as much as possible to render it nonleachable and innocuous, (d) reduction of wastes at the source, (e) recycling as much waste as is practical.

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2. Match the waste-recycling process or industry from the column on the left with the kind of material that can be recycled from the list on the right, below:

1. Recycle as raw material to the generator	(a) Waste alkali
2. Utilization for pollution control or waste treatment	(b) Hydraulic and lubricating oils
3. Energy production	(c) Incinerable materials
4. Materials with agricultural uses	(d) Incompletely consumed feedstock material
5. Organic substances	(e) Waste lime or phosphate-containing sludge

3. What material is recycled using hydrofinishing, treatment with clay, and filtration?

4. What is the "most important operation in solvent purification and recycle" that is used to separate solvents from impurities, water, and other solvents?

5. Dissolved air flotation (DAF) is used in the secondary treatment of wastes. What is the principle of this technique? For what kinds of hazardous-waste substances is it most applicable?

6. Match the process or industry from the column on the left with its "phase of waste treatment" from the list on the right, below:

1. Activated carbon sorption	(a) Primary treatment
2. Precipitation	(b) Secondary treatment
3. Reverse osmosis	(c) Polishing
4. Emulsion breaking	
5. Slurrying	

7. Distillation is used in treating and recycling a variety of wastes, including solvents, waste oil, aqueous phenolic wastes, and mixtures of ethylbenzene and styrene. What is the major hazardous-waste problem that arises from the use of distillation for waste treatment?

8. Supercritical fluid technology has a great deal of potential for the treatment of hazardous wastes. What are the principles involved with the use of supercritical fluids for waste treatment? Why is this technique especially advantageous? Which substance is most likely to be used as a supercritical fluid in this application? For which kinds of wastes are supercritical fluids most useful?

9. What are some advantages of using acetic acid, compared, for example, with sulfuric acid, as a neutralizing agent for treating waste alkaline materials?

10. Which of the following would be **least likely** to be produced by, or used as a reagent for the removal of heavy metals by their precipitation from solution? (a) Na_2CO_3, (b) CdS, (e) $Cr(OH)_3$, (d) KNO_3, (e) $Ca(OH)_2$

11. Both $NaBH_4$ and Zn are used to remove metals from solution. How do these substances remove metals? What are the forms of the metal products?

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12. Of the following, thermal treatment of wastes is **not** useful for (a) volume reduction, (b) destruction of heavy metals, (c) removal of volatile, combustible, mobile organic matter, (d) destruction of pathogenic materials, (e) destruction of toxic substances.
13. From the following, choose the waste liquid that is least amenable to incineration and explain why it is not readily incinerated: (a) methanol, (b) tetrachloroethylene, (c) acetonitrile, (d) toluene, (e) ethanol, (f) acetone.
14. Name and give the advantages of the process that is used to destroy more hazardous wastes by thermal means than are burned solely for the purpose of waste destruction.
15. What is the major advantage of fluidized-bed incinerators from the standpoint of controlling pollutant by-products?
16. What is the best way to obtain microorganisms to be used in the treatment of hazardous wastes by biodegradation?
17. What are the principles of composting? How is it used to treat hazardous wastes?
18. How is Portland cement used in the treatment of hazardous wastes for disposal? What might be some disadvantages of such a use?
19. What are the advantages of above ground disposal of hazardous wastes as opposed to burying wastes in landfills?
20. Describe and explain the best approach to managing leachate from hazardous-waste disposal sites.

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Manahan, Stanley E. "TOXICOLOGICAL CHEMISTRY"
Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC, 2001

23 TOXICOLOGICAL CHEMISTRY

23.1 INTRODUCTION TO TOXICOLOGY AND TOXICOLOGICAL CHEMISTRY

Ultimately, most pollutants and hazardous substances are of concern because of their toxic effects. To understand toxicological chemistry, it is essential to have some understanding of biochemistry, the science that deals with chemical processes and materials in living systems. Biochemistry is summarized in Chapter 10.

Toxicology

A **poison**, or **toxicant**, is a substance that is harmful to living organisms because of its detrimental effects on tissues, organs, or biological processes. **Toxicology** is the science of poisons. Toxicants to which subjects are exposed in the environment or occupationally may be in several different physical forms, such as vapors or dusts that are inhaled, liquids that can be absorbed through the skin, or solids ingested orally. A substance with which the toxicant may be associated (the solvent in which it is dissolved or the solid medium in which it is dispersed) is called the **matrix**. The matrix may have a strong effect upon the toxicity of the toxicant.

There are numerous variables related to the ways in which organisms are exposed to toxic substances. One of the most crucial of these, **dose,** is discussed in Section 23.2. Another important factor is the **toxicant concentration**, which may range from the pure substance (100%) down to a very dilute solution of a highly potent poison. Both the **duration** of exposure per incident and the **frequency** of exposure are important. The **rate** of exposure and the total time period over which the organism is exposed are both important situational variables. The exposure **site** and **route** also affect toxicity.

It is possible to classify exposures on the basis of four general categories. **Acute local** exposure occurs at a specific location over a time period of a few seconds to a few hours and may affect the exposure site, particularly the skin, eyes, or mucous membranes. The same parts of the body can be affected by **chronic local** exposure,

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for which the time span may be as long as several years. **Acute systemic** exposure is a brief exposure or exposure to a single dose and occurs with toxicants that can enter the body and affect organs that are remote from the entry site. **Chronic systemic** exposure differs in that the exposure occurs over a prolonged time period.

In discussing exposure sites for toxicants it is useful to consider the major routes and sites of exposure, distribution, and elimination of toxicants in the body, as shown in Figure 23.1. The major routes of accidental or intentional exposure to toxicants in humans and other animals are the skin (percutaneous route), the lungs (inhalation, respiration, pulmonary route), and the mouth (oral route). The pulmonary system is most likely to take in toxic gases or very fine, respirable solid or liquid particles. In other than a respirable form, a solid usually enters the body orally. Absorption through the skin is most likely for liquids, solutes in solution, and semisolids, such as sludges.

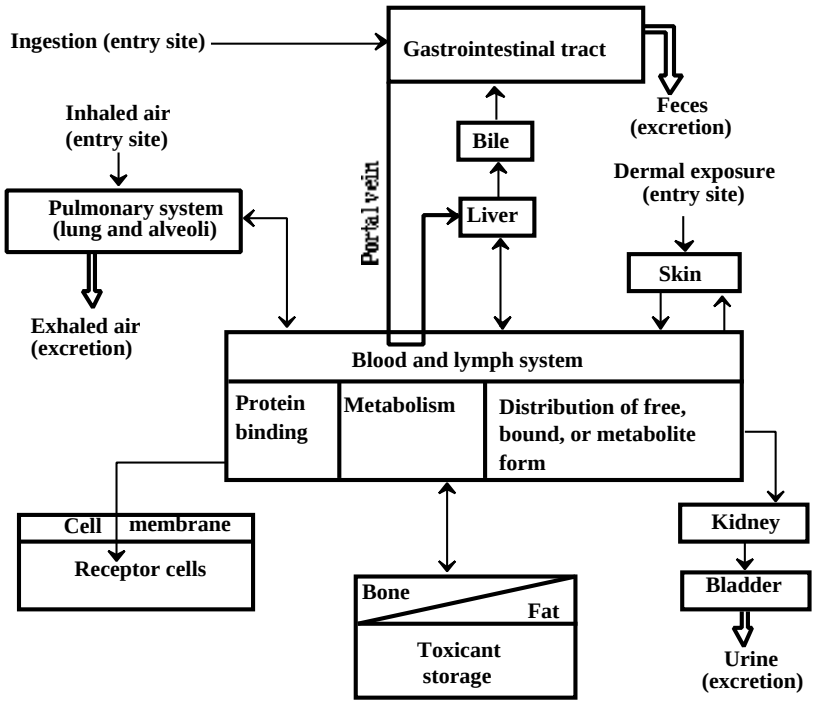


Figure 23.1 Major sites of exposure, metabolism, and storage, routes of distribution and elimination of toxic substances in the body.

The defensive barriers that a toxicant may encounter vary with the route of exposure. An interesting historical example of the importance of the route of exposure to toxicants is provided by cancer caused by contact of coal tar with skin. The permeability of skin is inversely proportional to the thickness of the skin's **stratum corneum** layer, which varies by location on the body in the following order: soles and palms > abdomen, back, legs, arms > genital (perineal) area. Evidence of the susceptibility of the genital area to absorption of toxic substances is to be found in accounts of the high incidence of cancer of the scrotum among chimney sweeps in London described by Sir Percival Pott, Surgeon General of Britain during the reign of King George III. The cancer-causing agent was coal tar

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condensed in chimneys. This material was more readily absorbed through the skin in the genital areas than elsewhere, leading to a high incidence of scrotal cancer. (The chimney sweeps' conditions were aggravated by their lack of appreciation of basic hygienic practices, such as bathing and regular changes of underclothing.)

Organisms can serve as indicators of various kinds of pollutants, thus serving as **biomonitors**. For example, higher plants, fungi, lichens, and mosses can be important biomonitors for heavy-metal pollutants in the environment.

Synergism, Potentiation, and Antagonism

The biological effects of two or more toxic substances can be different in kind and degree from those of one of the substances alone. Chemical interaction between substances may affect their toxicities. Both substances may act upon the same physiologic function, or two substances may compete for binding to the same receptor (molecule or other entity acted upon by a toxicant). When both substances have the same physiologic function, their effects may be simply **additive** or they may be **synergistic** (the total effect is greater than the sum of the effects of each separately). **Potentiation** occurs when an inactive substance enhances the action of an active one, and **antagonism** when an active substance decreases the effect of another active one.

23.2 DOSE-RESPONSE RELATIONSHIPS

Toxicants have widely varying effects upon organisms. Quantitatively, these variations include minimum levels at which the onset of an effect is observed, the sensitivity of the organism to small increments of toxicant, and levels at which the ultimate effect (particularly death) occurs in most exposed organisms. Some essential substances, such as nutrient minerals, have optimum ranges above and below which detrimental effects are observed (see Section 23.5 and Figure 23.4).

Factors such as those just outlined are taken into account by the **dose-response** relationship, which is one of the key concepts of toxicology. **Dose** is the amount, usually per unit body mass, of a toxicant to which an organism is exposed. **Response** is the effect upon an organism resulting from exposure to a toxicant. To define a dose-response relationship, it is necessary to specify a particular response, such as death of the organism, as well as the conditions under which the response is obtained, such as the length of time from administration of the dose. Consider a specific response for a population of the same kinds of organisms. At relatively low doses, none of the organisms exhibits the response (for example, all live), whereas at higher doses all of the organisms exhibit the response (for example, all die). In between, there is a range of doses over which some of the organisms respond in the specified manner and others do not, thereby defining a dose-response curve. Dose-response relationships differ among different kinds and strains of organisms, types of tissues, and populations of cells.

Figure 23.2 shows a generalized dose-response curve. The dose corresponding to the mid-point (inflection point) of the resulting S-shaped curve is the statistical estimate of the dose that would kill 50 % of the subjects. It is designated as LD_{50} and is commonly used to express toxicities.

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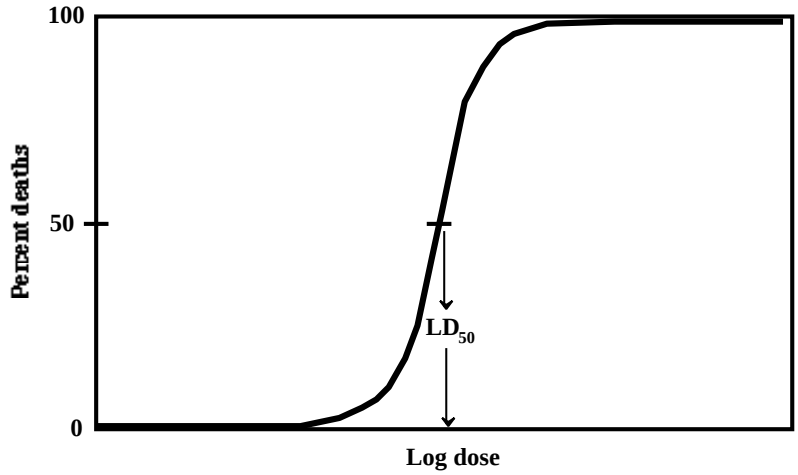


Figure 23.2 Illustration of a dose-response curve in which the response is the death of the organism. The cumulative percentage of deaths of organisms is plotted on the Y axis.

23.3 RELATIVE TOXICITIES

Table 23.1 illustrates standard **toxicity ratings** that are used to describe estimated toxicities of various substances to humans. In terms of fatal doses to an adult human of average size, a "taste" of a supertoxic substance (just a few drops or less) is fatal. A teaspoonful of a very toxic substance could have the same effect. However, as much as a quart of a slightly toxic substance might be required to kill an adult human.

When there is a substantial difference between LD_{50} values of two different substances, the one with the lower value is said to be the more **potent**. Such a comparison must assume that the dose-response curves for the two substances being compared have similar slopes.

Nonlethal Effects

So far, toxicities have been described primarily in terms of the ultimate effect—death of organisms, or lethality. This is obviously an irreversible consequence of exposure. In many, and perhaps most, cases, **sublethal** and **reversible** effects are of greater importance. The **margin of safety** (Figure 23.3) is used in connection with drugs to express the difference between the dose that gives a desired therapeutic effect and a harmful, potentially lethal, effect. This term applies to other substances, such as pesticides, for which it is desirable to have a large difference between the dose that kills a target species and that which harms a desirable species.

23.4 REVERSIBILITY AND SENSITIVITY

Sublethal doses of most toxic substances are eventually eliminated from an organism's system. If there is no lasting effect from the exposure, it is said to be **reversible**. In cases where the effect is permanent, it is termed **irreversible**. Irreversible effects of exposure remain after the toxic substance is eliminated from

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Table 23.1 Toxicity Scale with Example Substances[1]

Substance	Approximate LD_{50}	Toxicity rating
	10^5	1. Practically nontoxic $> 1.5 \times 10^4$ mg/kg
DEHP[2]		
Ethanol	10^4	2. Slightly toxic, 5×10^3 to 1.5×10^4 mg/kg
Sodium chloride		
Malathion	10^3	3. Moderately toxic, 500 to 5000 mg/kg
Chlordane		
Heptachlor	10^2	4. Very toxic, 50 to 500 mg/kg
Parathion	10	
TEPP[3]	1	5. Extremely toxic, 5 to 50 mg/kg
Tetrodotoxin[4]	10^{-1}	
	10^{-2}	6. Supertoxic, <5 mg/kg
TCDD[5]	10^{-3}	
	10^{-4}	
Botulinus toxin	10^{-5}	

[1] Doses are in units of mg of toxicant per kg of body mass. Toxicity ratings on the right are given as numbers ranging from 1 (practically nontoxic) through 6 (supertoxic) along with estimated lethal oral doses for humans in mg/kg. Estimated LD_{50} values for substances on the left have been measured in test animals, usually rats, and apply to oral doses.

[2] Bis(2-ethylhexyl)phthalate

[3] Tetraethylpyrophosphate

[4] Toxin from pufferfish

[5] TCDD represents 2,3,7,8,-tetrachlorodibenzodioxin, commonly called “dioxin.”

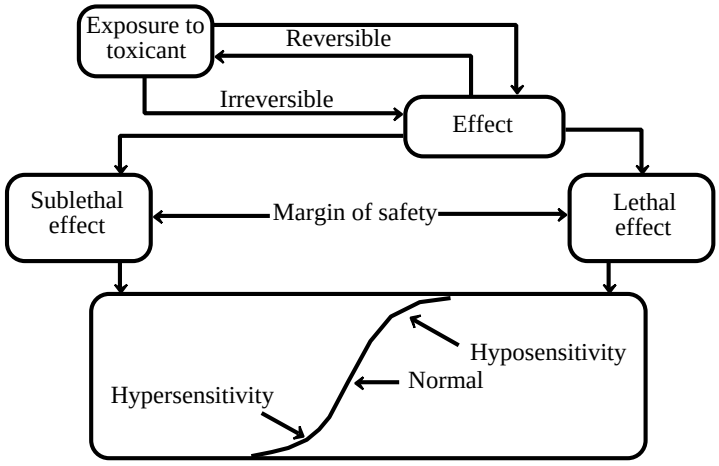


Figure 23.3 Effects of and responses to toxic substances.

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the organism. Figure 23.3 illustrates these two kinds of effects. For various chemicals and different subjects, toxic effects can range from the totally reversible to the totally irreversible.

Hypersensitivity and Hyposensitivity

Some subjects are very sensitive to a particular poison, whereas others are very resistant to the same substance. These two kinds of responses illustrate **hypersensitivity** and **hyposensitivity**, respectively; subjects in the mid-range of the dose-response curve are termed **normals**. These variations in response tend to complicate toxicology in that there is no specific dose guaranteed to yield a particular response, even in a homogeneous population.

In some cases, hypersensitivity is an induced response to exposure to a substance. After one or more doses of a chemical, a subject may develop an extreme reaction to it. This occurs with penicillin, for example, in cases where people develop such a severe allergic response to the antibiotic that exposure is fatal if countermeasures are not taken.

23.5 XENOBIOTIC AND ENDOGENOUS SUBSTANCES

Xenobiotic substances are those that are foreign to a living system, whereas those that occur naturally in a biologic system are termed **endogenous**. The levels of endogenous substances must usually fall within a particular concentration range for metabolic processes to occur normally. Levels below a normal range may result in a deficiency response or even death, and adverse effects may occur above the normal range. This kind of response is illustrated in Figure 23.4.

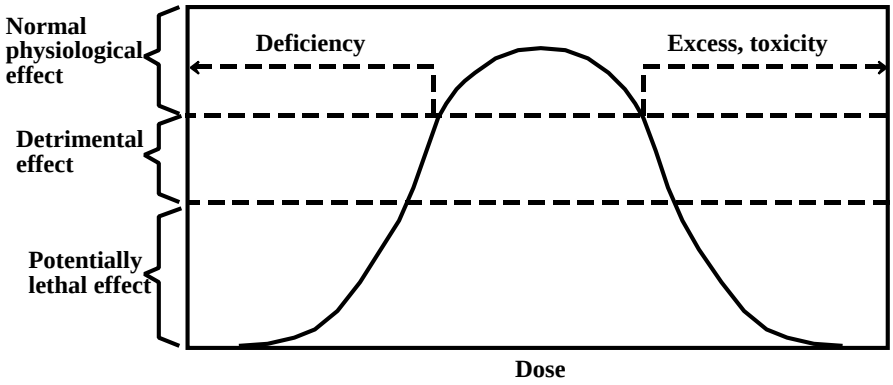


Figure 23.4 Biological effect of an endogenous substance in an organism showing optimum level, deficiency, and excess.

Examples of endogenous substances in organisms include various hormones, glucose (blood sugar), and some essential metal ions, including Ca^{2+}, K^{+}, and Na^{+}. The optimum level of calcium in human blood serum occurs over a rather narrow range of 9–9.5 milligrams per deciliter (mg/dL). Below these values, a deficiency response known as hypocalcemia occurs, manifested by muscle cramping. At serum

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levels above about 10.5 mg/dL hypercalcemia occurs, the major effect of which is kidney malfunction.

23.6 TOXICOLOGICAL CHEMISTRY

Toxicological Chemistry

Toxicological chemistry is the science that deals with the chemical nature and reactions of toxic substances, including their origins, uses, and chemical aspects of exposure, fates, and disposal.[1] Toxicological chemistry addresses the relationships between the chemical properties and molecular structures of molecules and their toxicological effects. Figure 23.5 outlines the terms discussed above and the relationships among them.

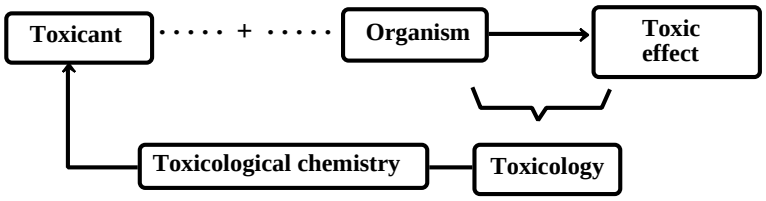


Figure 23.5 Toxicology is the science of poisons. Toxicological chemistry relates toxicology to the chemical nature of toxicants.

Toxicants in the Body

The processes by which organisms metabolize xenobiotic species are enzyme-catalyzed Phase I and Phase II reactions, which are described briefly here.[2,3]

Phase I Reactions

Lipophilic xenobiotic species in the body tend to undergo **Phase I reactions** that make them more water-soluble and reactive by the attachment of polar functional groups, such as –OH (Figure 23.6). Most Phase I processes are "microsomal mixed-function oxidase" reactions catalyzed by the cytochrome P-450 enzyme system that

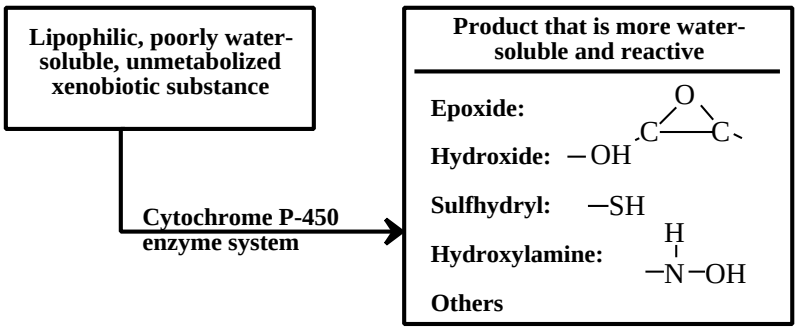


Figure 23.6 Illustration of Phase I reactions.

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is associated with the **endoplasmic reticulum** of the cell and occurring most abundantly in the liver of vertebrates.[4]

Phase II Reactions

A **Phase II reaction** occurs when an endogenous species is attached by enzyme action to a polar functional group which often, though not always, is the result of a Phase I reaction on a xenobiotic species. Phase II reactions**,** in which enzymes attach **conjugating agents** to xenobiotics, their Phase I reaction products, and nonxenobiotic compounds (Figure 23.7), are called **conjugation reactions**. The **conjugation product** of such a reaction is usually less toxic than the original xenobiotic compound, less lipid-soluble, more water-soluble, and more readily eliminated from the body. The major conjugating agents and the enzymes that catalyze their Phase II reactions are glucuronide (UDP glucuronyltransferase enzyme), glutathione (glutathionetransferase enzyme), sulfate (sulfotransferase enzyme), and acetyl (acetylation by acetyltransferase enzymes). The most abundant conjugation products are glucuronides. A glucuronide conjugate is illustrated in Figure 23.8, where -X-R represents a xenobiotic species conjugated to glucuronide, and R is an organic moiety. For example, if the xenobiotic compound conjugated is phenol, HXR is HOC_6H_5, X is the O atom, and R represents the phenyl group, C_6H_5.

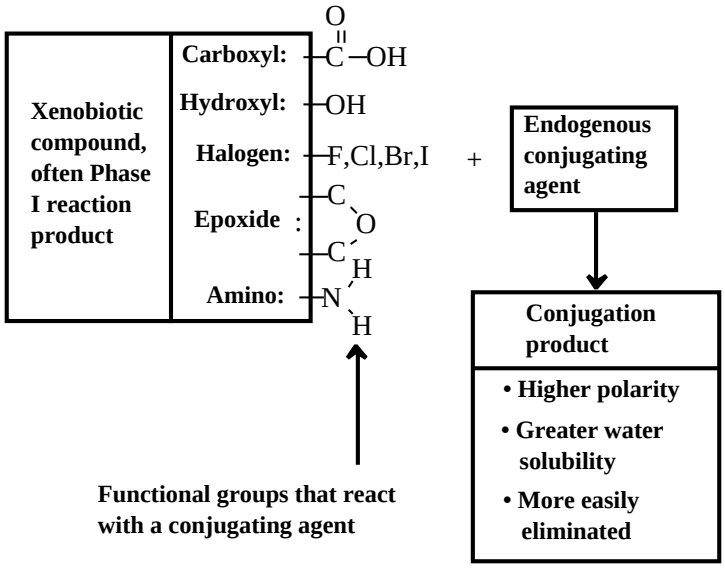


Figure 23.7 Illustration of Phase II reactions.

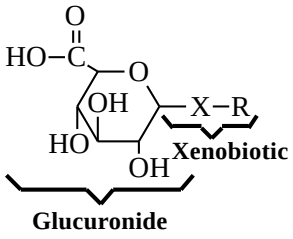


Figure 23.8 Glucuronide conjugate formed from a xenobiotic, HX-R.

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23.7 KINETIC PHASE AND DYNAMIC PHASE

Kinetic Phase

The major routes and sites of absorption, metabolism, binding, and excretion of toxic substances in the body are illustrated in Figure 23.1. Toxicants in the body are metabolized, transported, and excreted; they have adverse biochemical effects; and they cause manifestations of poisoning. It is convenient to divide these processes into two major phases, a kinetic phase and a dynamic phase.

In the **kinetic phase**, a toxicant or its metabolic precursor (**protoxicant**) may undergo absorption, metabolism, temporary storage, distribution, and excretion, as illustrated in Figure 23.9. A toxicant that is absorbed may be passed through the kinetic phase unchanged as an **active parent compound**, metabolized to a **detoxified metabolite** that is excreted, or converted to a toxic **active metabolite**. These processes occur through Phase I and Phase II reactions discussed above.

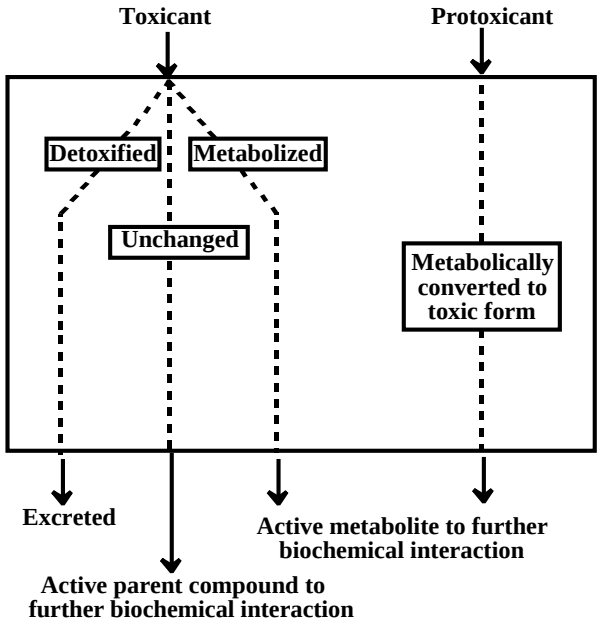


Figure 23.9 Processes involving toxicants or protoxicants in the kinetic phase.

Dynamic Phase

In the **dynamic phase** (Figure 23.10) a toxicant or toxic metabolite interacts with cells, tissues, or organs in the body to cause some toxic response. The three major subdivisions of the dynamic phase are the following:

- **Primary reaction** with a receptor or target organ
- A **biochemical response**
- **Observable effects**

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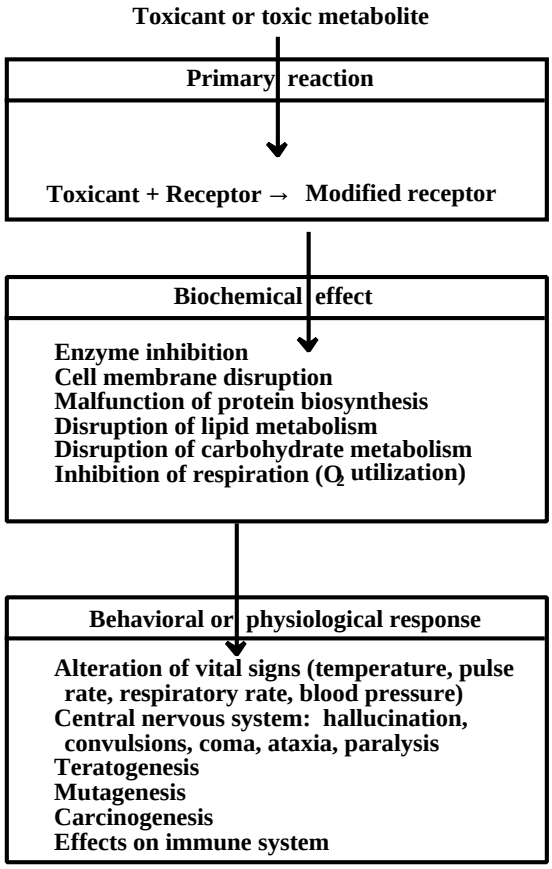


Figure 23.10 The dynamic phase of toxicant action.

Primary Reaction in the Dynamic Phase

A toxicant or an active metabolite reacts with a receptor. The process leading to a toxic response is initiated when such a reaction occurs. A typical example is when benzene epoxide, the initial product of the Phase I reaction of benzene (see Figure 23.16), forms an adduct with a nucleic acid unit in DNA (receptor) resulting in alteration of the DNA. (Many species that cause a toxic response are reactive intermediates, such as benzene epoxide, which have a brief lifetime but a strong tendency to undergo reactions leading to a toxic response while they are around.[5]) This reaction is an **irreversible** reaction between a toxicant and a receptor. A **reversible** reaction that can result in a toxic response is illustrated by the binding between carbon monoxide and oxygen-transporting hemoglobin (Hb) in blood to form carboxyhemoglobin, COHb, a process that causes hemoglobin to lose its capacity to transport oxygen, thus resulting in asphyxiation:

$$O_2Hb + CO \leftrightarrow COHb + O_2 \qquad (23.7.1)$$

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Biochemical Effects in the Dynamic Phase

The binding of a toxicant to a receptor may result in some kind of biochemical effect. The major ones are the following:

- Impairment of enzyme function by binding to the enzyme, coenzymes, metal activators of enzymes, or enzyme substrates
- Alteration of cell membrane or carriers in cell membranes
- Interference with carbohydrate metabolism
- Interference with lipid metabolism resulting in excess lipid accumulation ("fatty liver")
- Interference with respiration, the overall process by which electrons are transferred to molecular oxygen in the biological oxidation of energy-yielding substrates
- Stopping or interfering with protein biosynthesis by their action on DNA
- Interference with regulatory processes mediated by hormones or enzymes

Responses to Toxicants

Among the more immediate and readily observed manifestations of poisoning are alterations in the **vital signs** of **temperature**, **pulse rate**, **respiratory rate**, and **blood pressure**. Poisoning by some substances may cause an abnormal skin color (jaundiced, yellow skin from CCl_4 poisoning) or excessively moist or dry skin. Toxic levels of some materials or their metabolites cause the body to have unnatural **odors**, such as the bitter-almond odor of HCN in tissues of victims of cyanide poisoning. Symptoms of poisoning may be manifested by abnormal conditions of the eye or mouth. Gastrointestinal tract effects including pain, vomiting, or paralytic ileus (stoppage of the normal peristalsis movement of the intestines) occur as a result of poisoning by a number of toxic substances. Central nervous system poisoning may be manifested by **convulsions**, **paralysis**, **hallucinations**, and **ataxia** (lack of coordination of voluntary movements of the body), as well as abnormal behavior, including agitation, hyperactivity, disorientation, and delirium. Severe poisoning by some substances, including organophosphates and carbamates, causes **coma**, the term used to describe a lowered level of consciousness.

Prominent among the more chronic responses to toxicant exposure are mutations, cancer, and birth defects and effects on the immune system. Other observable effects, some of which may occur soon after exposure, include gastrointestinal illness, cardiovascular disease, hepatic (liver) disease, renal (kidney) malfunction, neurologic symptoms (central and peripheral nervous systems), and skin abnormalities (rash, dermatitis).

Often important effects of toxicant exposure are subclinical in nature and very difficult to detect. The most common of these are some kinds of damage to the immune system, chromosomal abnormalities, modification of functions of liver enzymes, and slowing of conduction of nerve impulses.

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23.8 TERATOGENESIS, MUTAGENESIS, CARCINOGENESIS, AND EFFECTS ON THE IMMUNE AND REPRODUCTIVE SYSTEMS

Teratogenesis

Teratogens cause birth defects. These usually arise from damage to embryonic or fetal cells. However, mutations in germ cells (egg or sperm cells) may cause birth defects such as Down's syndrome. The biochemical mechanisms by which teratogens act are varied. These include enzyme inhibition by xenobiotics; deprivation of the fetus of essential substrates, such as vitamins; interference with energy supply; or alteration of the permeability of the placental membrane.

Mutagenesis

Mutagens alter DNA to produce inheritable traits. Although mutation is a natural process that occurs even in the absence of xenobiotic substances, most mutations are harmful. The mechanisms of mutagenicity are similar to those of carcinogenicity, and mutagens often cause birth defects as well. Therefore, mutagenic hazardous substances are of major toxicological concern.

Biochemistry of Mutagenesis

To understand the biochemistry of mutagenesis, it is important to recall from Chapter 10 that DNA contains the nitrogenous bases adenine, guanine, cytosine, and thymine. The order in which these bases occur in DNA determines the nature and structure of newly produced RNA, a substance generated as a step in the synthesis of new proteins and enzymes in cells. Exchange, addition, or deletion of any of the nitrogenous bases in DNA alters the nature of RNA produced and can change vital life processes, such as the synthesis of an important enzyme. This phenomenon, which can be caused by xenobiotic compounds, is a mutation that can be passed on to progeny, usually with detrimental results.

There are several ways in which xenobiotic species can cause mutations. It is beyond the scope of this work to discuss these mechanisms in detail. For the most part, however, mutations due to xenobiotic substances are the result of chemical alterations of DNA, such as those discussed in the two examples below.

Nitrous acid, HNO_2, is an example of a chemical mutagen that is often used to cause mutations in bacteria. To understand the mutagenic activity of nitrous acid it should be noted that three of the nitrogenous bases—adenine, guanine, and cytosine—contain the amino group $–NH_2$. The action of nitrous acid is to replace amino groups with a hydroxy group. When this occurs, the DNA may not function in the intended manner, causing a mutation to occur.

Alkylation, the attachment of a small alkyl group, such as $-CH_3$ or $-C_2H_5$, to an N atom on one of the nitrogenous bases in DNA is one of the most common mechanisms leading to mutation. The methylation of "7" nitrogen in guanine in DNA to form N-Methylguanine is shown in Figure 23.11. O-alkylation can also occur by attachment of a methyl or other alkyl group to the oxygen atom in guanine.

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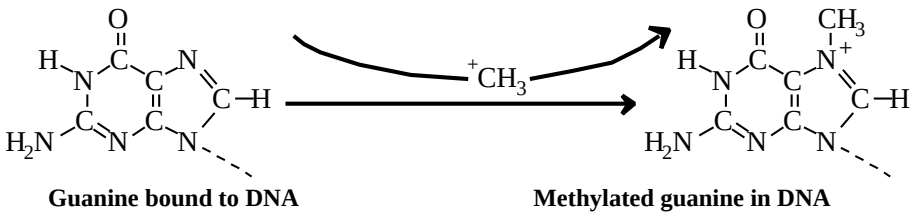


Figure 23.11 Alkylation of guanine in DNA.

A number of mutagenic substances act as alkylating agents. Prominent among these are the compounds shown in Figure 23.12.

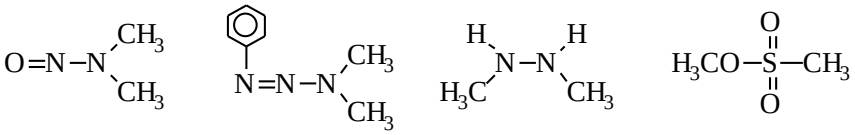
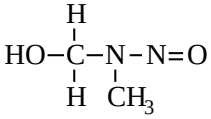
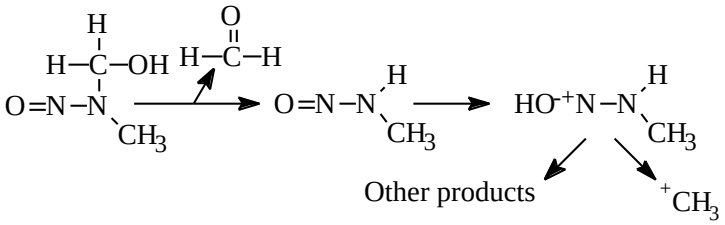


Figure 23.12 Examples of simple alkylating agents capable of causing mutations.

Alkylation occurs by way of generation of positively charged electrophilic species that bond to electron-rich nitrogen or oxygen atoms on the nitrogenous bases in DNA. The generation of such species usually occurs by way of biochemical and chemical processes. For example, dimethylnitrosamine (structure in Figure 23.12) is activated by oxidation through cellular NADPH to produce the following highly reactive intermediate:



This product undergoes several nonenzymatic transitions, losing formaldehyde and generating a methyl carbocation, $^{+}CH_3$, that can methylate nitrogenous bases on DNA



(23.7.1)

One of the more notable mutagens is tris(2,3-dibromopropyl)phosphate, commonly called “tris,” which was used as a flame retardant in children’s sleepwear. Tris was found to be mutagenic in experimental animals and metabolites of it were found in children wearing the treated sleepwear. This strongly suggested that tris is absorbed through the skin and its uses were discontinued.

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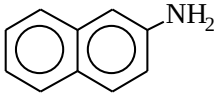
Carcinogenesis

Cancer is a condition characterized by the uncontrolled replication and growth of the body's own (somatic) cells. **Carcinogenic agents** can be categorized as follows:

- Chemical agents, such as nitrosamines and polycyclic aromatic hydrocarbons
- Biological agents, such as hepadnaviruses or retroviruses
- Ionizing radiation, such as X-rays
- Genetic factors, such as selective breeding.

Clearly, in some cases, cancer is the result of the action of synthetic and naturally occurring chemicals. The role of xenobiotic chemicals in causing cancer is called **chemical carcinogenesis**. It is often regarded as the single most important facet of toxicology and is clearly the one that receives the most publicity.

Chemical carcinogenesis has a long history. As noted earlier in this chapter, in 1775 Sir Percival Pott, Surgeon General serving under King George III of England, observed that chimney sweeps in London had a very high incidence of cancer of the scrotum, which he related to their exposure to soot and tar from the burning of bituminous coal. Around 1900 a German surgeon, Ludwig Rehn, reported elevated incidences of bladder cancer in dye workers exposed to chemicals extracted from coal tar; 2-naphthylamine,



was shown to be largely responsible. Other historical examples of carcinogenesis include observations of cancer from tobacco juice (1915), oral exposure to radium from painting luminescent watch dials (1929), tobacco smoke (1939), and asbestos (1960).

Biochemistry of Carcinogenesis

Large expenditures of effort and money on the subject in recent years have yielded a much better understanding of the biochemical bases of chemical carcinogenesis. The overall processes for the induction of cancer may be quite complex, involving numerous steps.[6] However, it is generally recognized that there are two major steps in carcinogenesis: an **initiation stage**, followed by a **promotional stage**. These steps are further subdivided as shown for the scheme of carcinogenesis in Figure 23.13.

Initiation of carcinogenesis may occur by reaction of a **DNA-reactive species** with DNA,[7] or by the action of an **epigenetic carcinogen** that does not react with DNA and is carcinogenic by some other mechanism. Most DNA-reactive species are **genotoxic carcinogens** because they are also mutagens. These substances react irreversibly with DNA. Cancer-causing substances that require metabolic activation are called **procarcinogens**. The metabolic species actually responsible for carcinogenesis is termed an **ultimate carcinogen**. Some species that are intermediate

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metabolites between precarcinogens and ultimate carcinogens are called **proximate carcinogens**. Carcinogens that do not require biochemical activation are categorized as **primary** or **direct-acting carcinogens**. Some procarcinogens and primary carcinogens are shown in Figure 23.14.

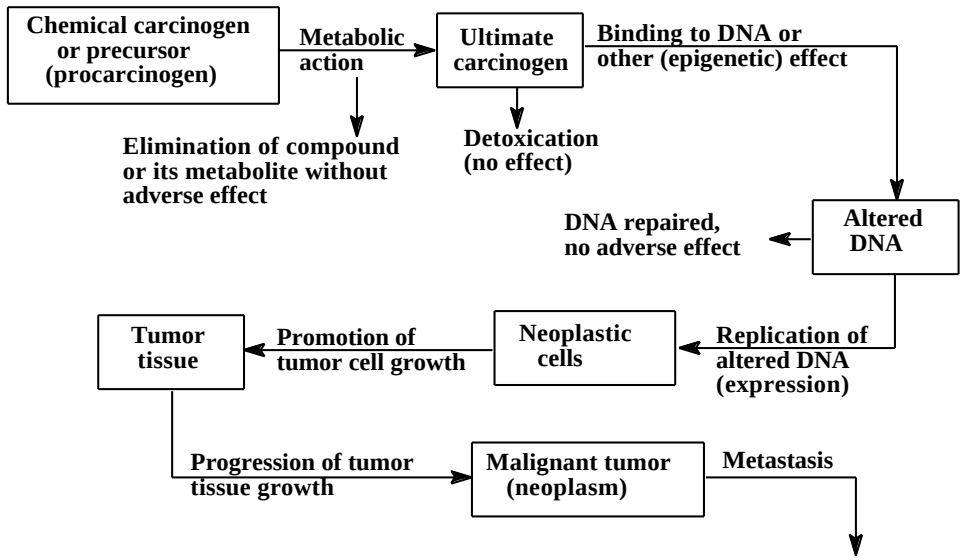
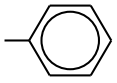


Figure 23.13 Outline of the process by which a carcinogen or procarcinogen may cause cancer.

Most substances classified as epigenetic carcinogens are **promoters** that act after initiation. Manifestations of promotion include increased numbers of tumor cells and decreased length of time for tumors to develop (shortened latency period). Promoters do not initiate cancer, are not electrophilic, and do not bind with DNA. The classic example of a promoter is a substance known chemically as decanoyl phorbol acetate or phorbol myristate acetate, which is extracted from croton oil.

Alkylating Agents in Carcinogenesis

Chemical carcinogens usually have the ability to form covalent bonds with macromolecular life molecules, especially DNA.[8] Prominent among the species that bond to DNA in carcinogenesis are the alkylating agents that attach alkyl groups—methyl (CH_3) or ethyl (C_2H_5)—to DNA. A similar type of compound, **arylating agents**, act to attach aryl moieties, such as the phenyl group

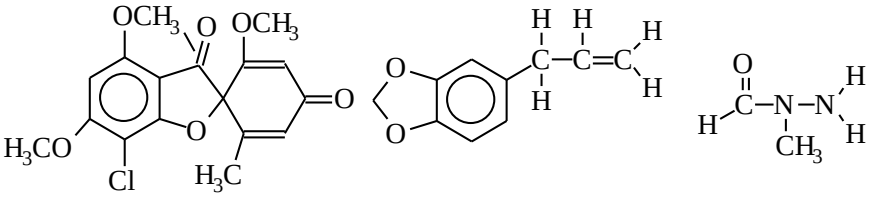

Phenyl group

to DNA. As shown by the examples in Figure 23.15, the alkyl and aryl groups become attached to N and O atoms in the nitrogenous bases that compose DNA. This alteration in DNA can trigger initiation of the sequence of events that results in the growth and replication of neoplastic (cancerous) cells. The reactive species that donate alkyl groups in alkylation are usually formed by metabolic activation by

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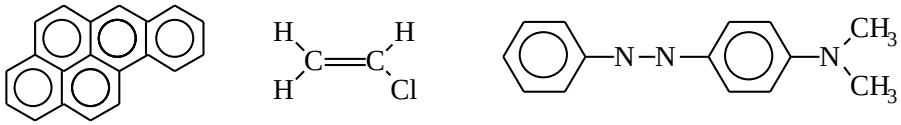
the action of enzymes. This process was shown for conversion of dimethylnitrosamine to a methylating metabolic intermediate in the discussion of mutagenesis earlier in this section.

Naturally occurring carcinogens that require bioactivation



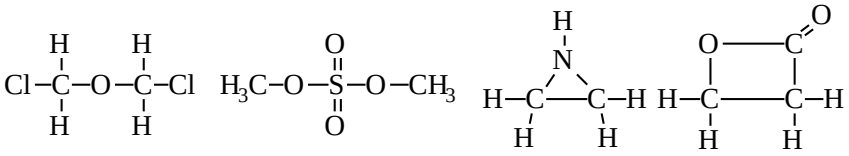
Griseofulvin (produced by *Penicillium griseofulvum*) **Saffrole (from sassafras)** **N-methyl-N-formylhydrazine (from edible false morel mushroom)**

Synthetic carcinogens that require bioactivation



Benzo(a)pyrene **Vinyl chloride** **4-Dimethylaminoazobenzene**

Primary carcinogens that do not require bioactivation



Bis(chloromethyl)-ether **Dimethyl sulfate** **Ethyleneimine** **β-Propioacetone**

Figure 23.14 Examples of the major classes of naturally occurring and synthetic carcinogens, some of which require bioactivation, and others that act directly.

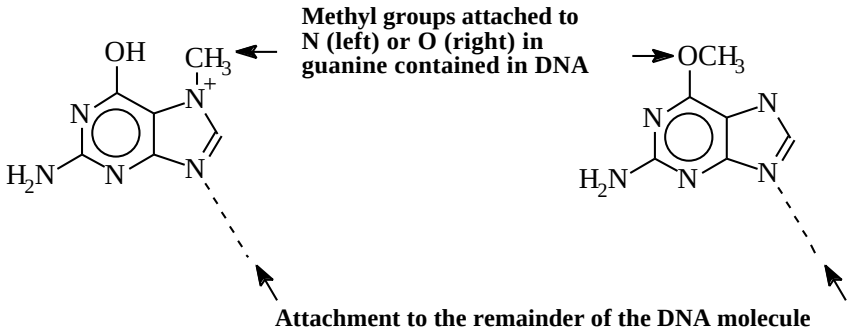


Figure 23.15 Alkylated (methylated) forms of the nitrogenous base guanine.

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Testing for Carcinogens

Only a few chemicals have definitely been established as human carcinogens. A well documented example is vinyl chloride, CH_2=CHCl, which is known to have caused a rare form of liver cancer (angiosarcoma) in individuals who cleaned autoclaves in the polyvinylchloride fabrication industry. In some cases, chemicals are known to be carcinogens from epidemiological studies of exposed humans. Animals are used to test for carcinogenicity, and the results can be extrapolated—although with much uncertainty—to humans.

Mutagenicity used to infer carcinogenicity is the basis of the **Bruce Ames** test, in which observations are made of the reversion of mutant histidine-requiring *Salmonella* bacteria back to a form that can synthesize its own histidine.[9] The test makes use of enzymes in homogenized liver tissue to convert potential procarcinogens to ultimate carcinogens. Histidine-requiring *Salmonella* bacteria are inoculated onto a medium that does not contain histidine, and those that mutate back to a form that can synthesize histidine establish visible colonies that are assayed to indicate mutagenicity.

According to Bruce Ames, the pioneer developer of the test that bears his name, animal tests for carcinogens that make use of massive doses of chemicals have a misleading tendency to give results that cannot be accurately extrapolated to assess cancer risks from smaller doses of chemicals.[10] This is because the huge doses of chemicals used kill large numbers of cells, which the organism's body attempts to replace with new cells. Rapidly dividing cells greatly increase the likelihood of mutations that result in cancer simply as the result of rapid cell proliferation, not genotoxicity.

Immune System Response

The **immune system** acts as the body's natural defense system to protect it from xenobiotic chemicals; infectious agents, such as viruses or bacteria; and neoplastic cells, which give rise to cancerous tissue. Adverse effects on the body's immune system are being increasingly recognized as important consequences of exposure to hazardous substances. Toxicants can cause **immunosuppression**, which is the impairment of the body's natural defense mechanisms. Xenobiotics can also cause the immune system to lose its ability to control cell proliferation, resulting in leukemia or lymphoma.

Another major toxic response of the immune system is **allergy** or **hypersensitivity**. This kind of condition results when the immune system overreacts to the presence of a foreign agent or its metabolites in a self-destructive manner. Among the xenobiotic materials that can cause such reactions are beryllium, chromium, nickel, formaldehyde, some kinds of pesticides, resins, and plasticizers.

Estrogenic Substances

A number of xenobiotic substances called exogenous estrogens are thought to have adverse effects on animal and human reproductive systems by mimicking or interfering with the action of estrogens (such as those in female sex hormone) and may cause disorders of the reproductive tract and effects such as reduced sperm

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counts and semen production.[11] Another effect of some concern is the potential to cause hormone-dependent cancers. A wide variety of synthetic compounds, including phthalates, alkylphenols, organochlorine compounds, and polycyclic aromatic hydrocarbons, are suspected of being exoestrogens.

23.9 ATSDR TOXICOLOGICAL PROFILES

A very useful source of information about the toxicological chemistry of various kinds of toxic substances is published by the U. S. Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry as ATSDR's Toxicological Profiles. These detailed documents are available on CD-ROM.[12] The substances covered are given in Table 23.2.

23.10 TOXIC ELEMENTS AND ELEMENTAL FORMS

Ozone, O_3, has several toxic effects. At 1 ppm by volume in air, ozone causes severe irritation and headache and irritates the eyes, upper respiratory system, and lungs. Inhalation of ozone can sometimes cause fatal pulmonary edema (abnormal accumulation of fluid in lung tissue). Ozone generates free radicals in tissue that can cause lipid peroxidation, oxidation of sulfhydryl (–SH) groups, and other destructive oxidation processes.

Elemental **white phosphorus** can enter the body by inhalation, by skin contact, or orally. It is a systemic poison, one that is transported through the body to sites remote from its entry site. White phosphorus causes anemia, gastrointestinal system dysfunction, bone brittleness, and eye damage. Exposure also causes **phossy jaw**, a condition in which the jawbone deteriorates and becomes fractured.

The most toxic of the elemental halogens is **fluorine** (F_2), a pale yellow, highly reactive gas that is a strong oxidant. It is a toxic irritant and attacks skin, eye tissue, and the mucous membranes of the nose and respiratory tract. **Chlorine** (Cl_2) gas reacts in water to produce a strongly oxidizing solution. This reaction is responsible for some of the damage caused to the moist tissue lining the respiratory tract when the tissue is exposed to chlorine. The respiratory tract is rapidly irritated by exposure to 10–20 ppm of chlorine gas in air, causing acute discomfort that warns of the presence of the toxicant. Even brief exposure to 1000 ppm of Cl_2 can be fatal. **Bromine** (Br_2), a volatile, dark red liquid that is toxic when inhaled or ingested, is strongly irritating to the mucous tissue of the respiratory tract and eyes and may cause pulmonary edema. Although it is irritating to the lungs, elemental solid **iodine** (I_2) has a very low vapor pressure of iodine, which limits exposure to its vapor.

Heavy Metals

Heavy metals are toxic in their chemically combined forms and some, notably mercury, are toxic in the elemental form. The toxic properties of some of the most hazardous heavy metals and metalloids are discussed here.

Although not truly a *heavy* metal, **beryllium** (atomic mass 9.01) is one of the more hazardous toxic elements. Its most serious toxic effect is berylliosis, a condition manifested by lung fibrosis and pneumonitis, which may develop after a latency

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Table 23.2 Materials Listed by ATSDR[13]

Acetone	1,2-Dibromoethane	Naphthalene
Acrolein	1,4-Dichlorobenzene	Nickel
Acrylonitrile	3,3'-Dichlorobenzidine	Nitrobenzene
Aldrin/Dieldrin	1,1-Dichloroethane	2-Nitrophenol/ 4-Nitrophenol
Alpha-,Beta-,Gamma- and Delta-Hexachloro-cyclohexane	1,2-Dichloroethane	Otto Fuels
	1,1-Dichloroethene	Pentachlorophenol
	1,2-Dichloroethene	Phenol
Aluminum	1,3-Dichloropropene	Plutonium
Ammonia	Diethyl Phthalate	Polybrominated Biphenyls
Arsenic	1,3-Dinitrobenzene/ 1,3,5-Trinitrobenzene	
Asbestos		Polychlorinated Biphenyls
Automotive Gasoline	Dinitrocresols	
Barium	Dinitrophenols	Polycyclic Aromatic Hydrocarbons (PAH's)
Benzene	2,4-Dinitrotoluene/ 2,6-Dinitrotoluene	
Benzidine		Radon
Beryllium	1,2-Diphenylhydrazine	RDX
Bis(2-Chloroethyl) Ether	Disulfoton	Selenium
Boron	Endosulfan	Silver
Bromomethane	Endrin	Stoddard Solvent
1,3-Butadiene	Ethylbenzene	1,1,2,2-Tetrachloroethane
2-Butanone	Ethylene Glycol and Propylene Glycol	Tetrachloroethylene
Cadmium		Tetryl
Carbon Disulfide	Fluorides, Hydrogen Fluoride, and Fluorine	Thallium
Carbon Tetrachloride		Thorium
Chlordane	Fuel Oils	Tin
Chlorobenzene	Heptachlor/Heptachlor Epoxide	Titanium Tetrachloride
Chlorodibenzofurans		Toluene
Chloroethane	Hexachlorobenzene	Toxaphene
Chloroform	Hexachlorobutadiene	1,1,1-Trichloroethane
Chloromethane	2-Hexanone	1,1,2-Trichloroethane
Chlorpyrifos	Hydraulic Fluids	Trichloroethylene
Chromium	Isophorone	2,4,6-Trichlorophenol
Coal Tar Pitch, and Coal Tar Pitch Volatiles	Jet Fuels (Jp4 And Jp7)	2,4,6-Trinitrotoluene
	Lead	Uranium
Cobalt	Manganese	Used Mineral-Based Crankcase Oil
Copper	Mercury	
Cresols: *o*-Cresol, *p*-Cresol, *m*-Cresol	Methoxychlor	Vanadium
	Methyl Parathion	Vinyl Acetate
Cyanide	Methyl Tert-Butyl Ether	Vinyl Chloride
4,4'-Ddt,4,4'-Dde,4,4'-Ddd	4, 4'-Methylenebis-(2-Chloroaniline) (MBOCA)	White Phosphorus
Di (2-Ethylhexyl) Phthalate		Wood Creosote, Coal Tar Creosote, Coal Tar
Di-N-Butylphthalate	Methylene Chloride	
Diazinon	Mirex And chlordecone	
1,2-Dibromo-3-Chloropropane	N-Nitrosodi-N-Propylamine	Xylenes
	N-Nitrosodiphenylamine	Zinc

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period of 5–20 years. Beryllium is a hypersensitizing agent and exposure to it causes skin granulomas and ulcerated skin. Beryllium was used in the nuclear weapons program in the U.S., and it is believed that 500 to 1000 cases of beryllium poisoning have occurred or will occur in the future as a result of exposure to workers. In July 1999, the U.S. Department of Energy acknowledged these cases of beryllium poisoning and announced proposed legislation to compensate the victims in a program expected to cost up to $15 million per year at its peak.

Cadmium adversely affects several important enzymes; it can also cause painful osteomalacia (bone disease) and kidney damage. Inhalation of cadmium oxide dusts and fumes results in cadmium pneumonitis characterized by edema and pulmonary epithelium necrosis (death of tissue lining lungs).

Lead, widely distributed as metallic lead, inorganic compounds, and organo-metallic compounds, has a number of toxic effects, including inhibition of the synthesis of hemoglobin. It also adversely affects the central and peripheral nervous systems and the kidneys. Its toxicological effects have been widely studied.

Arsenic is a metalloid that forms a number of toxic compounds. The toxic +3 oxide, As_2O_3, is absorbed through the lungs and intestines. Biochemically, arsenic acts to coagulate proteins, forms complexes with coenzymes, and inhibits the production of adenosine triphosphate (ATP), a key biochemical intermediate in essential metabolic processes involving the utilization of energy.

Arsenic is the toxic agent in one of the great environmental catastrophes of the last century, the result of its ingestion through well water in Bangladesh. Starting in the 1970s, several million wells were installed in Bangladesh to provide water free of pathogens. In 1992, a problem with arsenic contamination of many of the wells was shown to exist, and since that time tens of thousands of people have developed symptoms of arsenic poisoning from drinking the well water.

Elemental **mercury** vapor can enter the body through inhalation and be carried by the bloodstream to the brain, where it penetrates the blood-brain barrier. It disrupts metabolic processes in the brain causing tremor and psychopathological symptoms such as shyness, insomnia, depression, and irritability. Divalent ionic mercury, Hg^{2+}, damages the kidney.

23.11 TOXIC INORGANIC COMPOUNDS

Both **hydrogen cyanide** (HCN) and **cyanide salts** (which contain CN^- ion) are rapidly acting poisons; a dose of only 60–90 mg is sufficient to kill a human. Metabolically, cyanide bonds to iron(III) in iron-containing ferricytochrome oxidase enzyme (see enzymes in Chapter 10, Section 10.6), preventing its reduction to iron(II) in the oxidative phosphorylation process by which the body utilizes O_2. This prevents utilization of oxygen in cells, so that metabolic processes cease.

Carbon monoxide, **CO**, is a common cause of accidental poisonings. After it is inhaled, carbon monoxide enters the blood stream in the alveoli of the lungs. In the blood, it reacts with blood hemoglobin (Hb) to convert oxyhemoglobin (O_2Hb) to carboxyhemoglobin (COHb):

$$O_2Hb + CO \rightarrow COHb + O_2 \qquad (23.1.1)$$

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In this case, hemoglobin is the receptor (Section 23.7) acted on by the carbon monoxide toxicant. Carboxyhemoglobin is much more stable than oxyhemoglobin, so that its formation prevents hemoglobin from binding with oxygen and carrying it to body tissues.

The two most common toxic oxides of nitrogen are NO and NO_2. The more toxic nitrogen dioxide causes severe irritation of the innermost parts of the lungs, resulting in pulmonary edema. In cases of severe exposures, fatal bronchiolitis fibrosa obliterans may develop approximately 3 weeks after exposure to NO_2. Fatalities can result from even brief periods of inhalation of air containing 200–700 ppm of NO_2.

Nitrous oxide, N_2O is used as an oxidant gas and in dental surgery as a general anesthetic. This gas was once known as "laughing gas," and was used in the late 1800s as a "recreational gas" at parties held by some of our not-so-staid Victorian ancestors. Nitrous oxide is a central nervous system depressant and can act as an asphyxiant.

Hydrogen halides (general formula HX, where X is F, Cl, Br, or I) are relatively toxic gases. The most widely used of these gases are HF and HCl; their toxicities are discussed here.

Hydrogen fluoride, (HF, mp -83.1˚C, bp 19.5˚C) is used as a clear, colorless liquid or gas or as a 30–60% aqueous solution of **hydrofluoric acid**, both referred to here as HF. Both are extreme irritants to any part of the body that they contact, causing ulcers in affected areas of the upper respiratory tract. Lesions caused by contact with HF heal poorly, and tend to develop gangrene.

Fluoride ion, F^-, is toxic in soluble fluoride salts, such as NaF, causing **fluorosis**, a condition characterized by bone abnormalities and mottled, soft teeth. Livestock are especially susceptible to poisoning from fluoride fallout on grazing land; severely afflicted animals become lame and even die. Industrial pollution has been a common source of toxic levels of fluoride. However, about 1 ppm of fluoride used in some drinking water supplies prevents tooth decay.

Gaseous **hydrogen chloride** and its aqueous solution, called **hydrochloric acid**, both denoted as HCl, are much less toxic than HF. Hydrochloric acid is a natural physiological fluid present as a dilute solution in the stomachs of humans and other animals. However, inhalation of HCl vapor can cause spasms of the larynx as well as pulmonary edema and even death at high levels. The high affinity of hydrogen chloride vapor for water tends to dehydrate eye and respiratory tract tissue.

Silica (SiO_2, quartz) occurs in a variety of types of rocks such as sand, sandstone, and diatomaceous earth. **Silicosis**, a lung malady resulting from human exposure to silica dust from construction materials, sandblasting, and other sources, has been a common, disabling occupational disease.

Asbestos is the name given to a group of fibrous silicate minerals for which the approximate chemical formula is $Mg_3(Si_2O_5)(OH)_4$. Asbestos has been widely used in structural materials, brake linings, insulation, and pipe manufacture. Inhalation of asbestos may cause asbestosis (a pneumonia condition), mesothelioma (tumor of the mesothelial tissue lining the chest cavity adjacent to the lungs), and bronchogenic carcinoma (cancer originating with the air passages in the lungs) so that uses of asbestos have been severely curtailed and widespread programs have been undertaken to remove the material from buildings.

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Phosphine (PH_3), a colorless gas that undergoes autoignition at 100˚C, is a potential hazard in industrial processes and in the laboratory. Symptoms of poisoning from potentially fatal phosphine gas include pulmonary tract irritation, depression of the central nervous system, fatigue, vomiting, and difficult, painful breathing.

Tetraphosphorus decoxide, P_4O_{10}, is produced as a fluffy white powder from the combustion of elemental phosphorus, and reacts with water from air to form syrupy orthophosphoric acid, H_3PO_4. Because of the formation of acid by this reaction and its dehydrating action, P_4O_{10} is a corrosive irritant to skin, eyes and mucous membranes.

A colorless gas with a foul, rotten-egg odor, **hydrogen sulfide** is very toxic. In some cases, inhalation of H_2S kills faster than even hydrogen cyanide; rapid death ensues from exposure to air containing more than about 1000 ppm H_2S due to asphyxiation from respiratory system paralysis. Lower doses cause symptoms that include headache, dizziness, and excitement due to damage to the central nervous system. General debility is one of the numerous effects of chronic H_2S poisoning.

Sulfur dioxide, SO_2, dissolves in water to produce sulfurous acid, H_2SO_3; hydrogen sulfite ion, HSO_3^-; and sulfite ion, SO_3^{2-}. Because of its water solubility, sulfur dioxide is largely removed in the upper respiratory tract. It is an irritant to the eyes, skin, mucous membranes, and respiratory tract.

Number-one in synthetic chemical production, **sulfuric acid** (H_2SO_4) is a severely corrosive poison and dehydrating agent in the concentrated liquid form; it readily penetrates skin to reach subcutaneous tissue, causing tissue necrosis with effects resembling those of severe thermal burns. Sulfuric acid fumes and mists irritate eye and respiratory tract tissue, and industrial exposure has even caused tooth erosion in workers.

23.12 TOXIC ORGANOMETALLIC COMPOUNDS

Organometallic compounds are those in which metals are bound to carbon atoms in hydrocarbon groups or, in the case of carbonyls, to CO molecules. Widely used for a number of applications, organometallic compounds have a variety of toxic effects. They often behave in the body in ways totally unlike the inorganic forms of the metals that they contain, due in large part to the fact that, compared with inorganic forms, organometallic compounds have an organic nature, higher lipid solubility, and greater ability to penetrate cell membranes.

Perhaps the most notable toxic organometallic compound is **tetraethyllead**, $Pb(C_2H_5)_4$, a colorless, oily liquid that was widely used as a gasoline additive to boost octane rating. Tetraethyllead has a strong affinity for lipids and can enter the body by all three common routes of inhalation, ingestion, and absorption through the skin. Acting differently from inorganic compounds in the body, it affects the central nervous system with symptoms such as fatigue, weakness, restlessness, ataxia, psychosis, and convulsions.

The greatest number of organometallic compounds in commercial use are those of tin—tributyltin chloride and related tributyltin (TBT) compounds. These compounds have bactericidal, fungicidal, and insecticidal properties. They have particular environmental significance because of their widespread applications as industrial

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biocides, now increasingly limited because of their environmental and toxicological effects. Organotin compounds are readily absorbed through the skin, sometimes causing a skin rash. They probably bind with sulfur groups on proteins and appear to interfere with mitochondrial function.

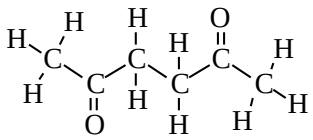
As discussed in Chapter 12, Section 12.3, methylated mercury species, CH_3Hg^+ and $(CH_3)_2Hg$, are produced by anaerobic bacteria. They are extremely toxic. Anaerobic bacteria also produce methylated forms of arsenic.

Metal carbonyls, regarded as extremely hazardous because of their toxicities, include nickel tetracarbonyl ($Ni(CO)_4$), cobalt carbonyl, and iron pentacarbonyl. Some of the hazardous carbonyls are volatile and readily taken into the body through the respiratory tract or through the skin. The carbonyls affect tissue directly and they break down to toxic carbon monoxide and products of the metal, which have additional toxic effects.

23.13 TOXICOLOGICAL CHEMISTRY OF ORGANIC COMPOUNDS

Alkane Hydrocarbons

Gaseous methane, ethane, propane, *n*-butane, and isobutane (both C_4H_{10}) are regarded as **simple asphyxiants** that form mixtures with air that contains insufficient oxygen to support respiration. The most common toxicological occupational problem associated with the use of hydrocarbon liquids in the workplace is dermatitis, caused by dissolution of the fat portions of the skin and characterized by inflamed, dry, scaly skin. Inhalation of volatile liquid 5–8 carbon *n*-alkanes and branched-chain alkanes may cause central nervous system depression, manifested by dizziness and loss of coordination. Exposure to *n*-hexane and cyclohexane results in loss of myelin (a fatty substance constituting a sheath around certain nerve fibers) and degeneration of axons (part of a nerve cell through which nerve impulses are transferred out of the cell). This has resulted in multiple disorders of the nervous system (**polyneuropathy**) including muscle weakness and impaired sensory function of the hands and feet. In the body, *n*-hexane is metabolized to 2,5-hexanedione:



2,5-hexanedione

This Phase I oxidation product can be observed in urine of exposed individuals and is used as a biological monitor of exposure to *n*-hexane.

Alkene and Alkyne Hydrocarbons

Ethylene, a widely used colorless gas with a somewhat sweet odor, acts as a simple asphyxiant and anesthetic to animals and is phytotoxic (toxic to plants). The toxicological properties of propylene ($H_2C{=}CHCH_3$) are very similar to those of ethylene. Colorless, odorless, gaseous 1,3-butadiene ($H_2C{=}CHCH{=}CH_2$) is an irritant to eyes and respiratory system mucous membranes; at higher levels it can

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cause unconsciousness and even death. Acetylene, H-C≡C-H, is a colorless gas with a garlic odor that acts as an asphyxiant and narcotic, causing headache, dizziness, and gastric disturbances.

Benzene and Aromatic Hydrocarbons

Inhaled benzene is readily absorbed by blood, from which it is strongly taken up by fatty tissues. For the non-metabolized compound, the process is reversible and benzene is excreted through the lungs. As shown in Figure 23.16, benzene is converted to phenol by a Phase I oxidation reaction (see Section 23.6) in the liver. The reactive and short-lived benzene epoxide intermediate known to occur in this reaction is probably responsible for much of the unique toxicity of benzene, which involves damage to bone marrow. In addition to phenol, several other oxygenated derivatives of benzene are produced when it is metabolized, as is *trans*,*trans*-muconic acid, produced by cleavage of the benzene ring.

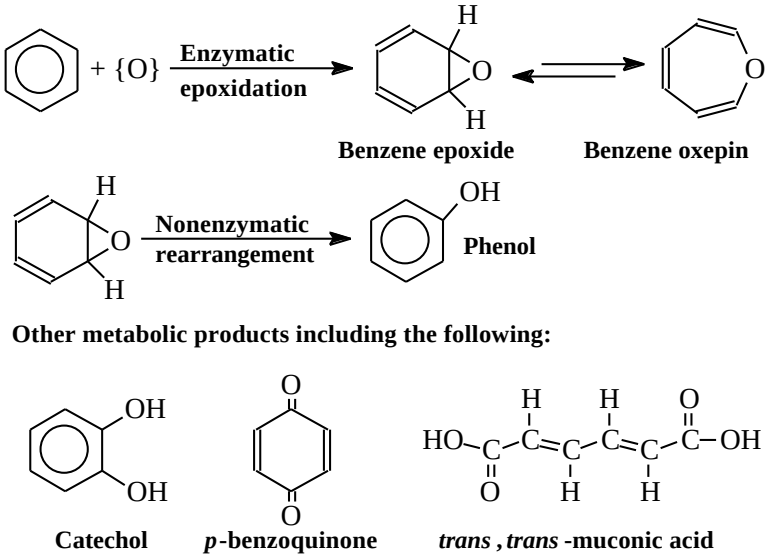


Figure 23.16 Conversion of benzene to phenol in the body.

Benzene is a skin irritant, and progressively higher local exposures can cause skin redness (erythema), burning sensations, fluid accumulation (edema), and blistering. Inhalation of air containing about 7 g/m^3 of benzene causes acute poisoning within an hour because of a narcotic effect upon the central nervous system manifested progressively by excitation, depression, respiratory system failure, and death. Inhalation of air containing more than about 60 g/m^3 of benzene can be fatal within a few minutes.

Long-term exposures to lower levels of benzene cause nonspecific symptoms, including fatigue, headache, and appetite loss. Chronic benzene poisoning produces blood abnormalities, including a lowered white cell count, an abnormal increase in blood lymphocytes (colorless corpuscles introduced to the blood from the lymph glands), anemia, a decrease in the number of blood platelets required for clotting

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(thrombocytopenia), and damage to bone marrow. It is thought that preleukemia, leukemia, or cancer may result.

Toluene, a colorless liquid boiling at 101.4˚C, is classified as moderately toxic through inhalation or ingestion; it has a low toxicity by dermal exposure. Because it possesses an aliphatic -CH_3 side chain that can be oxidized enzymatically to products that are readily excreted from the body (see the metabolic reaction scheme in Figure 23.17), toluene is much less toxic than benzene.

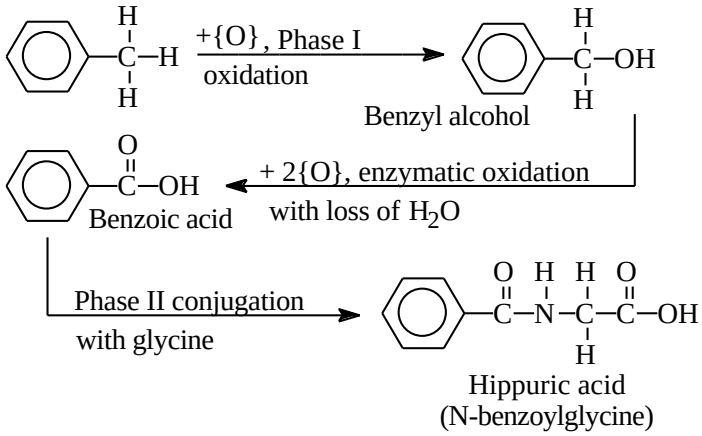


Figure 23.17 Metabolic oxidation of toluene with conjugation to hippuric acid, which is excreted with urine.

Benzo[a]pyrene is the most studied of the **polycyclic aromatic hydrocarbons** (PAHs). Some metabolites of PAH compounds, particularly the 7,8-diol-9,10-epoxide of benzo[a]pyrene shown in Figure 23.18, are known to cause cancer. There are two stereoisomers of this metabolite, both of which are known to be potent mutagens and presumably can cause cancer.

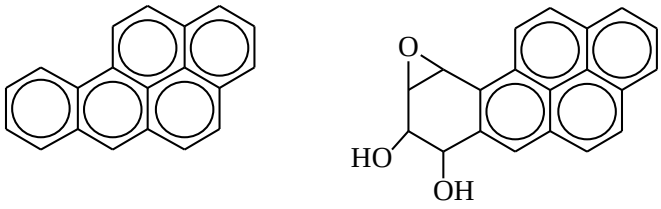
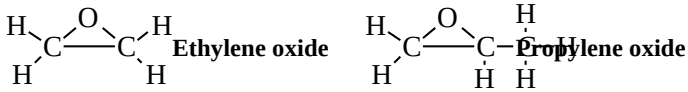


Figure 23.18 Benzo[a]pyrene and its carcinogenic metabolic product.

Oxygen-Containing Organic Compounds

Hydrocarbon **oxides** such as ethylene oxide and propylene oxide,



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which are characterized by an epoxide functional group bridging oxygen between two adjacent C atoms, are significant for both their uses and their toxic effects. Ethylene oxide, a gaseous, colorless, sweet-smelling, flammable, explosive gas used as a chemical intermediate, sterilant, and fumigant, has a moderate to high toxicity, is a mutagen, and is carcinogenic to experimental animals. Inhalation of relatively low levels of this gas results in respiratory tract irritation, headache, drowsiness, and dyspnea, whereas exposure to higher levels causes cyanosis, pulmonary edema, kidney damage, peripheral nerve damage, and even death. Propylene oxide is a colorless, reactive, volatile liquid (bp 34˚C) with uses similar to those of ethylene oxide and similar, though less severe, toxic effects.

Human exposure to the three light alcohols shown in Figure 23.19. is common because they are widely used industrially and in consumer products.

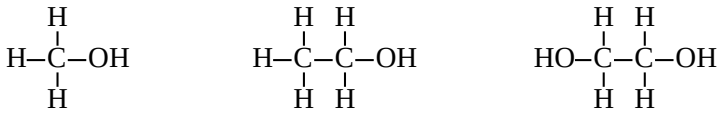


Figure 23.19 **Alcohols** such as these three compounds are oxygenated compounds in which the hydroxyl functional group is attached to an alkyl or alkenyl hydrocarbon skeleton.

Methanol, which has caused many fatalities when ingested accidentally or consumed as a substitute for beverage ethanol, is metabolically oxidized to formaldehyde and formic acid. In addition to causing acidosis, these products affect the central nervous system and the optic nerve. Acute exposure to lethal doses causes an initially mild inebriation, followed in about 10–20 hours by unconsciousness, cardiac depression, and death. Sublethal exposures can cause blindness from deterioration of the optic nerve and retinal ganglion cells.

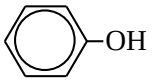
Ethanol is usually ingested through the gastrointestinal tract, but can be absorbed as vapor by the alveoli of the lungs. This alcohol is oxidized metabolically, first to acetaldehyde (discussed later in this section), then to CO_2. Ethanol has numerous acute effects resulting from central nervous system depression. These range from decreased inhibitions and slowed reaction times at 0.05% blood ethanol, through intoxication, stupor, and—at more than 0.5% blood ethanol—death. Ethanol also has a number of chronic effects, of which the addictive condition of alcoholism and cirrhosis of the liver are the most prominent.

Despite its widespread use in automobile cooling systems, exposure to **ethylene glycol** is limited by its low vapor pressure. However, inhalation of droplets of ethylene glycol can be very dangerous. In the body, ethylene glycol initially stimulates the central nervous system, then depresses it. Glycolic acid, chemical formula $HOCH_2CO_2H$, formed as an intermediate metabolite in the metabolism of ethylene glycol, may cause acidemia, and oxalic acid produced by further oxidation may precipitate in the kidneys as solid calcium oxalate, CaC_2O_4, causing clogging.

Although the first antiseptic used on wounds and in surgery, **phenol** is a protoplasmic poison that damages all kinds of cells. The acute toxicological effects of phenol are largely upon the central nervous system and death can occur as soon as one-half hour after exposure. Acute poisoning by phenol can cause severe gastro-

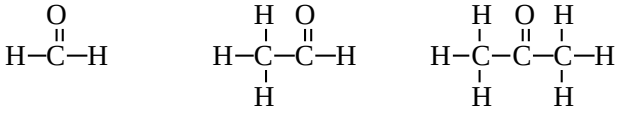
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intestinal disturbances, kidney malfunction, circulatory system failure, lung edema, and convulsions. Fatal doses of phenol can be absorbed through the skin. Key organs damaged by chronic phenol exposure include the spleen, pancreas, and kidneys. The toxic effects of other phenols resemble those of phenol.



Phenol

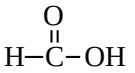
Aldehydes and ketones, such as the following,



Formaldehyde **Acetaldehyde** **Acetone**

are compounds that contain the carbonyl (C=O) group. **Formaldehyde** is uniquely important because of its widespread use and toxicity. In the pure form, formaldehyde is a colorless gas with a pungent, suffocating odor. It is commonly encountered as **formalin,** a 37–50% aqueous solution of formaldehyde containing some methanol. Exposure to inhaled formaldehyde via the respiratory tract is usually due to molecular formaldehyde vapor, whereas exposure by other routes is usually due to formalin. Prolonged, continuous exposure to formaldehyde can cause hypersensitivity. A severe irritant to the mucous membrane linings of both the respiratory and alimentary tracts, formaldehyde reacts strongly with functional groups in molecules. Formaldehyde has been shown to be a lung carcinogen in experimental animals. The toxicity of formaldehyde is largely due to its metabolic oxidation product, formic acid (see below). Colorless, liquid acetaldehyde acts as an irritant and systemically as a narcotic to the central nervous system. The ketones, such as acetone are relatively less toxic than the aldehydes. Pleasant-smelling acetone can act as a narcotic; it causes dermatitis by dissolving fats from skin.

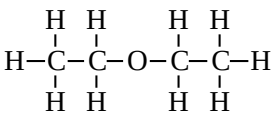
Formic acid,



Formic acid

is a relatively strong acid that is corrosive to tissue. In Europe, decalcifier formulations that contain about 75% formic acid are sold for removing mineral scale, and children ingesting these solutions have suffered corrosive lesions to mouth and esophageal tissue. Although acetic acid, CH_3CO_2H, as a 4–6% solution in vinegar is an ingredient of many foods, pure acetic acid (glacial acetic acid) is extremely corrosive to tissue that it contacts.

The common **ethers**, such as diethyl ether,



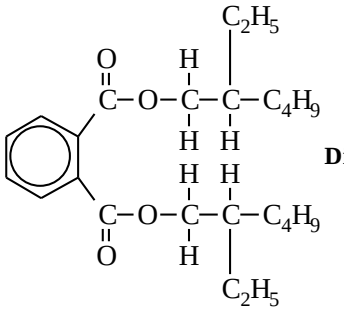
Diethyl ether

have relatively low toxicities because of the low reactivity of the C–O–C functional group which has very strong carbon-oxygen bonds. Exposure to volatile diethyl ether

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is usually by inhalation and about 80% of this compound that gets into the body is eliminated unmetabolized as the vapor through the lungs. Diethyl ether depresses the central nervous system and is a depressant widely used as an anesthetic for surgery. Low doses of diethyl ether cause drowsiness, intoxication, and stupor, whereas higher exposures cause unconsciousness and even death.

Insofar as potential health effects are concerned, **di-(2-ethylhexyl) phthalate** (DEHP)



Di-(2-ethylhexyl) phthalate

is arguably the ester of most concern. This is because of the use of this ester at levels of around 30% as a plasticizer to impart flexibility to poly(vinyl chloride) (PVC) plastic. As a consequence of the widespread use of DEHP-containing PVC plastics, DEHP has become a ubiquitous contaminant found in water, sediment, food, and biological samples. The most acute concern arises from its use in medical applications, particularly bags used to hold intravenous solutions administered to medical patients. As a result of medical use, DEHP enters the blood of hemophiliacs, kidney dialysis patients, and premature and high-risk infants. Although the acute toxic effects of DEHP are low, such widespread direct exposure of humans is worrisome.

Organonitrogen Compounds

Organonitrogen compounds constitute a large group of compounds with diverse toxicities. Examples of several of the kinds of organonitrogen compounds discussed here are given in Figure 23.20.

The lower **amines**, such as the methylamines, are rapidly and easily taken into the body by all common exposure routes. They are basic and react with water in tissue,

$$R_3N + H_2O \rightarrow R_3NH^+ + OH^- \qquad (23.13.1)$$

raising the pH of the tissue to harmful levels, acting as corrosive poisons (especially to sensitive eye tissue), and causing tissue necrosis at the point of contact. Among the systemic effects of amines are necrosis (tissue death) of the liver and kidneys, lung hemorrhage and edema, and sensitization of the immune system. The lower amines are among the more toxic substances in routine, large-scale use.

Ethylenediamine is the most common of the **alkyl polyamines**, compounds in which two or more amino groups are bonded to alkane moieties. Its toxicity rating is only 3, but it is a strong skin sensitizer and can damage eye tissue.

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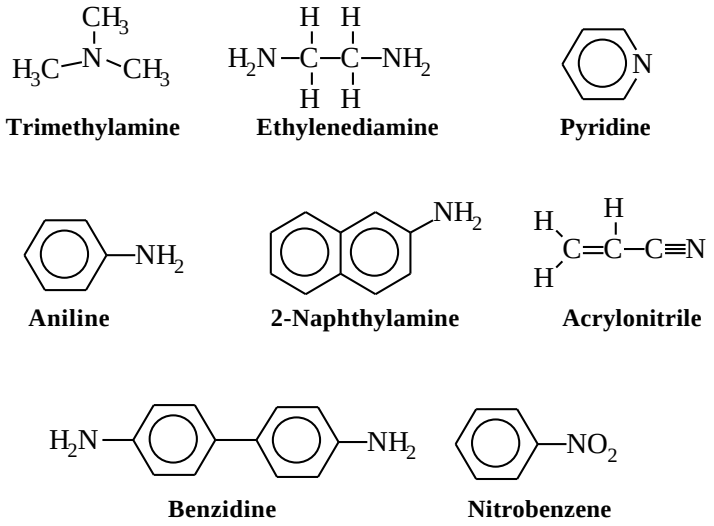


Figure 23.20 Some toxicologically significant organonitrogen compounds.

Aniline is a widely used industrial chemical and is the simplest of the **carbocyclic aromatic amines**, a class of compounds in which at least one substituent group is an aromatic hydrocarbon ring bonded directly to the amino group. There are numerous compounds with many industrial uses in this class of amines. Some of the carbocyclic aromatic amines have been shown to cause cancer in the human bladder, ureter, and pelvis, and are suspected of being lung, liver, and prostate carcinogens. A very toxic colorless liquid with an oily consistency and distinct odor, aniline readily enters the body by inhalation, ingestion, and through the skin. Metabolically, aniline converts iron(II) in hemoglobin to iron(III). This causes a condition called **methemoglobinemia**, characterized by cyanosis and a brown-black color of the blood, in which the hemoglobin can no longer transport oxygen in the body. This condition is not reversed by oxygen therapy.

Both **1-naphthylamine** (α-naphthylamine) and **2-naphthylamine** (β-naphthylamine) are proven human bladder carcinogens. In addition to being a proven human carcinogen, **benzidine**, 4,4'-diaminobiphenyl, is highly toxic and has systemic effects that include blood hemolysis, bone marrow depression, and kidney and liver damage. It can be taken into the body orally, by inhalation into the lungs, and by skin sorption.

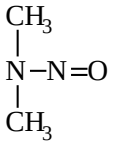
Nitriles contain the -C≡N functional group. Colorless liquid **acetonitrile**, CH_3CN, is widely used in the chemical industry. With a toxicity rating of 3–4, acetonitrile is considered relatively safe, although it has caused human deaths, perhaps by metabolic release of cyanide. **Acrylonitrile**, a colorless liquid with a peach-seed (cyanide) odor, is highly reactive because it contains both nitrile and C=C groups. Ingested, absorbed through the skin, or inhaled as vapor, acrylonitrile metabolizes to release deadly HCN, which it resembles toxicologically.

The simplest of the **nitro compounds**, **nitromethane** H_3CNO_2, is an oily liquid that causes anorexia, diarrhea, nausea, and vomiting, and damages the kidneys and

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liver. **Nitrobenzene**, a pale yellow, oily liquid with an odor of bitter almonds or shoe polish, can enter the body by all routes. It has a toxic action much like that of aniline, converting hemoglobin to methemoglobin, which cannot carry oxygen to body tissue. Nitrobenzene poisoning is manifested by cyanosis.

N-nitroso compounds (**nitrosamines**) contain the N–N=O functional group and have been found in a variety of materials to which humans may be exposed, including beer, whiskey, and cutting oils used in machining. Cancer may result from exposure to a single large dose or from chronic exposure to relatively small doses of some nitrosamines. Dimethylnitrosamine was once widely used as an industrial solvent and was known to cause liver damage and jaundice in exposed workers. Studies initiated in the 1950s showed that dimethylnitrosamine is a carcinogenic compound.



Dimethylnitrosamine (N-nitrosodimethylamine)

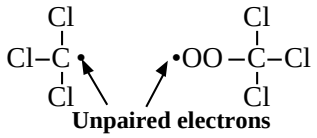
Isocyanates and Methyl Isocyanate

Compounds with the general formula R–N=C=O (R is a hydrocarbon group) are **isocyanates**, widely used industrial chemicals noted for the high chemical and metabolic reactivity of their characteristic functional group. **Methyl isocyanate**, $H_3C–N=C=O$, was the toxic agent involved in the catastrophic industrial poisoning in Bhopal, India, on December 2, 1984, the worst industrial accident in history. In this incident several tons of methyl isocyanate were released, killing 2000 people and affecting about 100,000. The lungs of victims were attacked; survivors suffered long-term shortness of breath and weakness from lung damage, as well as numerous other toxic effects including nausea and bodily pain.

Organohalide Compounds

The toxicities of alkyl halides, such as carbon tetrachloride, CCl_4, vary a great deal with the compound. Most of these compounds cause depression of the central nervous system, and individual compounds exhibit specific toxic effects.

During its many years of use as a consumer product, carbon tetrachloride compiled a grim record of toxic effects that led the U.S. Food and Drug Administration (FDA) to prohibit its household use in 1970. It is a systemic poison that affects the nervous system when inhaled, and the gastrointestinal tract, liver, and kidneys when ingested. The biochemical mechanism of carbon tetrachloride toxicity involves reactive radical species, including

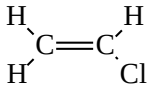


that react with biomolecules, such as proteins and DNA. The most damaging such reaction occurs in the liver as **lipid peroxidation**, consisting of the attack of free

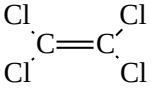
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radicals on unsaturated lipid molecules, followed by oxidation of the lipids through a free radical mechanism.

The most significant **alkenyl** or **olefinic organohalides** are the lighter chlorinated compounds, such as vinyl chloride and tetrachloroethylene:



Vinyl chloride



Tetrachloroethylene

Because of their widespread use and disposal in the environment, the numerous acute and chronic toxic effects of the alkenyl halides are of considerable concern.

The central nervous system, respiratory system, liver, and blood and lymph systems are all affected by vinyl chloride exposure, which has been widespread because of this compound's use in poly(vinyl chloride) manufacture. Most notably, vinyl chloride is carcinogenic, as discussed in Section 23.8. Tetrachloroethylene damages the liver, kidneys, and central nervous system. It is a suspected human carcinogen.

Individuals exposed to irritant monochlorobenzene by inhalation or skin contact suffer symptoms to the respiratory system, liver, skin, and eyes. Ingestion of this compound causes effects similar to those of toxic aniline, including incoordination, pallor, cyanosis, and eventual collapse.

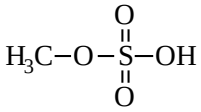
Because of their once widespread use in electrical equipment, as hydraulic fluids, and in many other applications, polychlorinated biphenyls (PCBs, see Chapter 12, Section 12.12, and the structures in Figure 12.10.) became widespread, extremely persistent environmental pollutants. PCBs have a strong tendency to undergo bioaccumulation in lipid tissue.

Organosulfur compounds

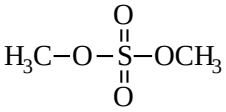
Not all organosulfur compounds are particularly toxic. Their hazards are often reduced by their strong, offensive odors that warn of their presence.

Inhalation of even very low concentrations of the alkyl **thiols**, such as methanethiol, H_3CSH, can cause nausea and headaches; higher levels can cause increased pulse rate, cold hands and feet, and cyanosis. In extreme cases, unconsciousness, coma, and death occur. Like H_2S, the alkyl thiols are precursors to cytochrome oxidase poisons.

An oily, water-soluble liquid, **methylsulfuric acid** is a strong irritant to skin, eyes, and mucous tissue. Colorless, odorless **dimethyl sulfate** is highly toxic and is a



Methylsulfuric acid



Dimethylsulfate

primary carcinogen that does not require bioactivation to cause cancer. Skin or

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mucous membranes exposed to dimethyl sulfate develop conjunctivitis and inflammation of nasal tissue and respiratory tract mucous membranes following an initial latent period during which few symptoms are observed. Damage to the liver and kidneys, pulmonary edema, cloudiness of the cornea, and death within 3–4 days can result from heavier exposures.

Organophosphorus Compounds

Organophosphorus compounds have varying degrees of toxicity. Some of these compounds, such as the "nerve gases" produced as industrial poisons, are deadly in minute quantities. The most toxicologically significant organophosphorous compounds are the organophosphates, examples of which are shown in Figure 23.21.

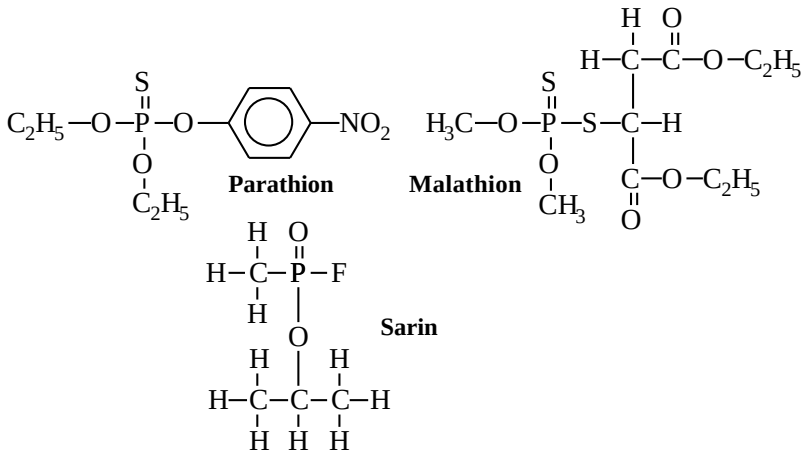


Figure 23.21 Some organophosphates.

Organophosphate esters have been widely used as insecticides. Phosphate esters containing the P=S (thiono) group, as in parathion and malathion shown in Figure 23.21, exhibit higher insect:mammal toxicity ratios than their nonsulfur analogs. Environmentally, organophosphate insecticides are superior to many of the organochlorine insecticides because the organophosphates readily undergo biodegradation and do not bioaccumulate.

The first commercially successful organophosphate insecticide was **parathion**, first licensed for use in 1944. This insecticide has a toxicity rating of 6 (supertoxic). Since its use began, several hundred people have been killed by parathion. As little as 120 mg of parathion has been known to kill an adult human, and a dose of 2 mg has been fatal to a child. Most accidental poisonings have occurred by absorption through the skin. Methylparathion (a closely related compound with methyl groups instead of ethyl groups) is regarded as extremely toxic, and in August 1999 the U.S. Environmental Protection Agency proposed severely curtailing its use.

Malathion is the best known of the phosphorodithioate insecticides, which have 2 sulfur atoms attached to phosphate. It has a relatively high insect:mammal toxicity ratio because of its two carboxyester linkages that are hydrolyzable by carboxylase enzymes (possessed by mammals, but not insects) to relatively nontoxic products. For example, although malathion is a very effective insecticide, its LD_{50} for adult

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male rats is about 100 times that of parathion.

Powerful inhibitors of acetylcholinesterase enzyme, organophosphorus "nerve gas" military poisons include **Sarin** (Figure 23.21) and **VX**. A systemic poison to the central nervous system that is readily absorbed as a liquid through the skin, Sarin may be lethal at doses as low as about 0.0l mg/kg; a single drop can kill a human.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

A poison, or toxicant, is a substance that is [1]_____ _____. Toxicology is defined as [2]_____. Based on duration and location, exposure can be divided into the four categories of [3]_____. Organisms that serve as indicators of various kinds of pollutants are called [4]_____ _____. When two toxicants have greater physiologic effects together than the sum of the two separately, their effects are said to be [5]_____. [6]_____ _____ occurs when an inactive substance enhances the action of an active one, and [7]_____ when an active substance decreases the effect of another active one. [8]_____ is the amount to which an organism is exposed and the observed effect, such as death of the organism is given the term [9] . The dose at which half of test subjects are killed is denoted [10]_____. The difference between the effective and lethal dose of a toxic substances employed for useful purposes, such as pharmaceutical uses is called the [11]_____ _____. If there is no lasting effect from a toxic substance, the effect is said to be [12]_____, whereas if the effect is permanent, it is termed [13]_____. Very high susceptibility to a poison is called [14]_____ whereas very high resistance to the same substance is called [15]_____. [16]_____ substances are those that are foreign to a living system, whereas those that occur naturally in a biologic system are termed [17]_____. Toxicological chemistry is defined as [18]_____ _____. Phase I reactions convert potentially toxic substances to [19]_____ _____ substances by [20]_____ _____. Most Phase I processes are catalyzed by [21]_____. Phase II reactions are called [22]_____ in which enzymes attach [23]_____ _____ to xenobiotics, their Phase I reaction products, and nonxenobiotic compounds. The most abundant conjugation products are [24]_____ _____. In the [25]_____ phase, a toxicant or protoxicant may undergo absorption, metabolism, temporary storage, distribution, and excretion. In the [26]_____ phase, the major divisions of which are [27]_____

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_____,
an actual toxic effect occurs and is manifested. Major biochemical effects of the binding of a toxicant to a receptor are [28]_____

_____.
Among the more immediate and readily observed manifestations of poisoning are alterations in [29]_____. Central nervous system poisoning may be manifested by [30]_____
_____. Teratogens cause [31]_____. Mutagens alter DNA to produce [32]_____. This commonly occurs by attachment of [33]_____ to nitrogenous bases in DNA. Four major classes of carcinogenic agents are [34]_____
_____. A historically significant example of chemical carcinogenesis reported in England in 1775 is cancer of the [35]_____ caused by exposure to [36]_____
_____. The two major steps in carcinogenesis are [37]_____
_____. A procarcinogen is a compound that is [38]_____ to an ultimate carcinogen, whereas a chemical species that does not require such a conversion is called a [39]_____
_____ carcinogen. Carcinogens that act on DNA are usually [40]_____
_____ agents. An organochlorine compound known to be a human carcinogen is [41]_____. Mutagenicity to bacteria used to infer carcinogenicity is the basis of the [42]_____ test. Two major responses of the immune system to toxicants are [43]_____
_____. A class of toxic substances that are thought to adversely affect animal and human reproductive systems by mimicking or interfering with the action of hormones are the [44]_____. ATSDR is known for its publication of very useful [45]_____. A particularly toxic form of elemental oxygen is [46]_____ and a toxic form of elemental phosphorus is [47]_____. Elemental fluorine is a toxic [48]_____
that attacks [49]_____
_____. Cadmium, lead, and mercury are all examples of toxic [50]_____. Exposure to cyanide prevents the body from utilizing [51]_____ whereas inhalation of carbon monoxide prevents [52]_____
_____. Nitrous oxide is a [53]_____ depressant and can act as [54]_____. Asbestos consists of a group of [55]_____
_____, inhalation of which can cause pneumonia-like asbestosis as well as [56]_____. Foul smelling hydrogen sulfide can kill by causing [57]_____
_____. The most notable toxic organometallic compound is [58]_____ formerly used as [59]_____
_____. The greatest number of organometallic compounds in commercial use are those of [60]_____. Anaerobic bacteria can produce methylated organometallic compounds of [61]_____.
Nickel forms a very toxic compound with metal-carbon bonds belonging to the class of [62]_____. Gaseous methane, ethane, propane, *n*-butane, and

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isobutane are regarded toxicologically as [63]_____. Exposure to *n*-hexane and cyclohexane results in damage to [64]_____ tissue that can result in a condition known as [65]_____. Benzene is metabolized to produce a reactive and short-lived [66]_____ intermediate, and exposure to this aromatic hydrocarbon can damage [67]_____ and perhaps cause [68]_____. Toluene is much less toxic than benzene because it possesses a [69]_____ that is oxidized to make a product that is conjugated to produce [70]_____. Benzo[a]pyrene can be converted metabolically to the [71]_____ which is a potent [72]_____ and presumably can cause [73]_____. A sublethal, but devastating effect of methanol ingestion is [74]_____ _____. Ingestion of ethylene glycol can cause clogging of [75]_____ _____. A protoplasmic poison once widely used as an antiseptic is [76] .

Prolonged, continuous exposure to formaldehyde can cause [77]_____. An ester to which humans are exposed because of its use in plastics in medical equipment is [78]_____. Exposure to aniline may cause [79]_____. Both 1-naphthylamine and 2-naphthylamine are proven [80]_____. Exposure to some N-nitroso compounds (nitrosamines) can cause [81]_____. The biochemical mechanism of carbon tetrachloride toxicity involves [82]_____ species. Toxicologically, vinyl chloride causes [83]_____. Toxicologically dimethyl sulfate is [84]_____. The most toxicological significant organophosphorous compounds are [85]_____ _____.

Answers to Chapter Summary

1. harmful to living organisms because of its detrimental effects on tissues, organs, or biological processes
2. the science of poisons
3. acute local, chronic local, acute systemic, and chronic systemic
4. biomonitors
5. synergistic
6. Potentiation
7. antagonism
8. Dose
9. response
10. LD_{50}
11. margin of safety
12. reversible
13. irreversible
14. hypersensitivity
15. hyposensitivity
16. Xenobiotic
17. endogenous
18. the science that deals with the chemical nature and reactions of toxic substances,

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including their origins, uses, and chemical aspects of exposure, fates, and disposal
19. more water-soluble and reactive
20. the attachment of polar functional groups, such as –OH
21. the cytochrome P-450 enzyme system
22. conjugation reactions
23. conjugating agents
24. glucuronides
25. kinetic
26. dynamic
27. a primary reaction, a biochemical response, and observable effects
28. impairment of enzyme function, alteration of cell membrane, interference with carbohydrate metabolism, interference with lipid metabolism, interference with respiration, stopping or interfering with protein biosynthesis, and interference with regulatory processes
29. vital signs
30. convulsions, paralysis, hallucinations, ataxia, and coma
31. birth defects
32. inheritable traits
33. alkyl groups such as the methyl group
34. chemical agents, biological agents, ionizing radiation, and genetic factors
35. scrotum
36. coal tar and soot
37. an initiation stage followed by a promotional stage
38. converted metabolically
39. primary or direct-acting
40. alkylating or arylating
41. vinyl chloride
42. Bruce Ames
43. immunosuppression and hypersensitivity
44. exoestrogens
45. Toxicological Profiles
46. ozone
47. white phosphorus
48. irritant
49. skin, eye tissue, and the mucous membranes of the nose and respiratory tract
50. heavy metals
51. oxygen
52. oxygen transport by hemoglobin in blood
53. central nervous system
54. an asphyxiant
55. fibrous silicate minerals
56. respiratory tract cancer
57. asphyxiation from respiratory system paralysis
58. tetraethyllead
59. a gasoline additive to boost octane rating
60. tin

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61. mercury and arsenic
62. carbonyls
63. simple asphyxiants
64. nerve
65. polyneuropathy
66. benzene epoxide
67. bone marrow
68. leukemia
69. methyl group
70. hippuric acid
71. 7,8-diol-9,10-epoxide
72. mutagen
73. cancer
74. blindness caused by damage to the optic nerve
75. kidneys
76. phenol
77. hypersensitivity
78. di-(2-ethylhexyl) phthalate
79. methemoglobinemia
80. human bladder carcinogens
81. cancer
82. reactive radical
83. liver cancer
84. a primary carcinogen
85. the organophosphates

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QUESTIONS AND PROBLEMS

1. How are conjugating agents and Phase II reactions involved with some toxicants?
2. What is the toxicological importance of proteins, particularly as related to protein structure?

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3. What is the toxicological importance of lipids? How are lipids related to hydrophobic pollutants and toxicants?
4. What are Phase I reactions? What enzyme system carries them out? Where is this enzyme system located in the cell?
5. Name and describe the science that deals with the chemical nature and reactions of toxic substances, including their origins, uses, and chemical aspects of exposure, fates, and disposal.
6. What is a dose-response curve?
7. What is meant by a toxicity rating of 6?
8. What are the three major subdivisions of the *dynamic phase* of toxicity, and what happens in each?
9. Characterize the toxic effect of carbon monoxide in the body. Is its effect reversible or irreversible? Does it act on an enzyme system?
10. Of the following, choose the one that is **not** a biochemical effect of a toxic substance: (a) impairment of enzyme function by binding to the enzyme, (b) alteration of cell membrane or carriers in cell membranes, (c) change in vital signs, (d) interference with lipid metabolism, (e) interference with respiration.
11. Distinguish among teratogenesis, mutagenesis, carcinogenesis, and immune system effects. Are there ways in which they are related?
12. As far as environmental toxicants are concerned, compare the relative importance of acute and chronic toxic effects and discuss the difficulties and uncertainties involved in studying each.

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24 INDUSTRIAL ECOLOGY, RESOURCES, AND ENERGY

24.1 INTRODUCTION

Modern civilization depends upon a wide variety of resources consisting largely of minerals that are processed to recover the materials needed for industrial activities. The most common type of mineral material so used, and one that all people depend upon for their existence, is soil, used to grow plants for food. Also of crucial importance are metal ores. Some of these metal sources are common and abundant, such as iron ore; others, such as sources of chromium, are rare and will not last long at current rates of consumption. There are also some crucial sources of nonmetals. Sulfur, for example, is abundant and extracted in large quantities as a by-product of sulfur-rich fuels. Phosphorus, a key fertilizer element, will last only for several generations at current rates of consumption.

The materials needed for modern societies can be provided from either **extractive** (nonrenewable) or **renewable** sources. Extractive industries remove irreplaceable mineral resources from the earth's crust. The utilization of mineral resources is strongly tied with technology, energy, and the environment. Perturbations in one usually cause perturbations in the others. For example, reductions in automotive exhaust pollutant levels to reduce air pollution have made use of catalytic devices that require platinum-group metals, a valuable and irreplaceable natural resource. Furthermore, automotive pollution control devices result in greater gasoline consumption than would be the case if exhaust emissions were not a consideration (a particularly pronounced effect in the earlier years of emissions control). The availability of many metals depends upon the quantity of energy used and the amount of environmental damage tolerated in the extraction of low-grade ores. Many other such examples could be cited. Because of these intimate interrelationships, technology, resources, and energy must all be considered together. The practice of industrial ecology has a significant potential to improve environmental quality with reduced consumption of nonrenewable resources and energy.

In discussing nonrenewable sources of minerals and energy, it is useful to define

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two terms related to available quantities. The first of these is **resources**, defined as quantities that are estimated to be *ultimately* available. The second term is **reserves**, which refers to well-identified resources that can be profitably utilized with existing technology.

24.2 MINERALS IN THE GEOSPHERE

There are numerous kinds of mineral deposits that are used in various ways. These are, for the most part, sources of metals which occur in **batholiths** composed of masses of igneous rock that have been extruded in a solid or molten state into the surrounding rock strata. In addition to deposits formed directly from solidifying magma, associated deposits are produced by water interacting with magma. Hot aqueous solutions associated with magma can form rich **hydrothermal** deposits of minerals. Several important metals, including lead, zinc, and copper, are often associated with hydrothermal deposits.

Some useful mineral deposits are formed as **sedimentary deposits** along with the formation of sedimentary rocks. **Evaporites** are produced when seawater is evaporated. Common mineral evaporites are halite (NaCl), sodium carbonates, potassium chloride, gypsum ($CaSO_4 \cdot 2H_2O$), and magnesium salts. Many significant iron deposits consisting of hematite (Fe_2O_3) and magnetite (Fe_3O_4) were formed as sedimentary bands when earth's atmosphere was changed from reducing to oxidizing as photosynthetic organisms produced oxygen, precipitating the oxides from the oxidation of soluble Fe^{2+} ion.

Deposition of suspended rock solids by flowing water can cause segregation of the rocks according to differences in size and density. This can result in the formation of useful **placer** deposits that are enriched in desired minerals. Gravel, sand, and some other minerals, such as gold, often occur in placer deposits.

Some mineral deposits are formed by the enrichment of desired constituents when other fractions are weathered or leached away. The most common example of such a deposit is bauxite, Al_2O_3, remaining after silicates and other more soluble constituents have been dissolved by the weathering action of water under the severe conditions of hot tropical climates with very high levels of rainfall. This kind of material is called a **laterite.**

Evaluation of Mineral Resources

To make its extraction worthwhile, a mineral must be enriched at a particular location in earth's crust relative to the average crustal abundance. Normally applied to metals, such an enriched deposit is called an **ore**. The value of an ore is expressed in terms of a **concentration factor**:

$$\text{Concentration factor} = \frac{\text{Concentration of material in ore}}{\text{Average crustal concentration}} \qquad (24.2.1)$$

Obviously, higher concentration factors are always desirable. Required concentration factors decrease with average crustal concentrations and with the value of the commodity extracted. A concentration factor of 4 might be adequate for iron, which makes up a relatively high percentage of earth's crust. Concentration factors must be

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several hundred or even several thousand for less expensive metals that are not present at very high percentages in earth's crust. However, for an extremely valuable metal, such as platinum, a relatively low concentration factor is acceptable because of the high financial return obtained from extracting the metal.

Acceptable concentration factors are a sensitive function of the price of a metal. Shifts in price can cause significant changes in which deposits are mined. If the price of a metal increases by, for example, 50%, and the increase appears to be long term, it becomes profitable to mine deposits that had not been mined previously. The opposite can happen, as is often the case when substitute materials are found or newly discovered, richer sources go into production.

In addition to large variations in the concentration factors of various ores, there are extremes in the geographic distribution of mineral resources. The United States is perhaps about average for all nations in terms of its mineral resources, possessing significant resources of copper, lead, iron, gold, and molybdenum, but virtually without resources of some important strategic metals, including chromium, tin, and platinum-group metals. For its size and population, South Africa is particularly blessed with some important metal mineral resources.

24.3 EXTRACTION AND MINING

Minerals are usually extracted from Earth's crust by various kinds of mining procedures, but other techniques can be employed as well. The raw materials so obtained include inorganic compounds such as phosphate rock, sources of metal such as lead sulfide ore, clay used for firebrick, and structural materials, such as sand and gravel.

Surface mining, which can consist of digging large holes in the ground, or strip mining, is used to extract minerals that occur near the surface. A common example of surface mining is quarrying of rock. Vast areas have been dug up to extract coal. Because of past mining practices, surface mining got a well-deserved bad name. With modern reclamation practices, however, topsoil is first removed and stored. After the mining is complete, the topsoil is spread on top of overburden that has been replaced such that the soil surface has gentle slopes and proper drainage. Topsoil spread over the top of the replaced spoil, often carefully terraced to prevent erosion, is seeded with indigenous grass and other plants, fertilized, and watered, if necessary, to provide vegetation. The end result of carefully done **mine reclamation** projects is a well-vegetated area suitable for wildlife habitat, recreation, forestry, grazing, and other beneficial purposes.

Extraction of minerals from placer deposits formed by deposition from water has obvious environmental implications. Mining of placer deposits can be accomplished by dredging from a boom-equipped barge. Another means that can be used is hydraulic mining with large streams of water. One interesting approach for more coherent deposits is to cut the ore with intense water jets, then suck up the resulting small particles with a pumping system. These techniques have a high potential to pollute water and disrupt waterways.

For many minerals, underground mining is the only practical means of extraction. An underground mine can be very complex and sophisticated. The structure of the mine depends upon the nature of the deposit. It is, of course, necessary to have a shaft

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that reaches to the ore deposit. Horizontal tunnels extend out into the deposit, and provision must be made for sumps to remove water and for ventilation. Factors that must be considered in designing an underground mine include the depth, shape, and orientation of the ore body, as well as the nature and strength of the rock in and around it; thickness of overburden; and depth below the surface.

Usually, significant amounts of processing are required before a mined product is used or even moved from the mine site. Such processing, and the by-products of it, can have significant environmental effects. Even rock to be used for aggregate and for road construction must be crushed and sized, a process that has the potential to emit air-polluting dust particles into the atmosphere. Crushing is also a necessary first step for further processing of ore. Some minerals occur to an extent of a few percent or even less in the rock taken from the mine and must be concentrated on site so that the residue does not have to be hauled far. For metals mining, these processes—as well as roasting, extraction—and similar operations, are covered under the category of **extractive metallurgy**.

One of the more environmentally troublesome by-products of mineral refining consists of waste **tailings**. By the nature of the mineral processing operations employed, tailings are usually finely divided and, as a result, subject to chemical weathering processes. Heavy metals associated with metal ores can be leached from tailings, producing water runoff contaminated with cadmium, lead, and other pollutants. Adding to the problem are some of the processes used to refine ore. Large quantities of cyanide solution are used in some processes to extract low levels of gold from ore, posing obvious toxicological hazards.

Environmental problems resulting from exploitation of extractive resources—including disturbance of land, air pollution from dust and smelter emissions, and water pollution from disrupted aquifers—are aggravated by the fact that the general trend in mining involves utilization of less rich ore. This is illustrated in Figure 24.1, showing the average percentage of copper in copper ore mined since 1900. The average percentage of copper in ore mined in 1900 was about 4%, but by 1982 it was about 0.6% in domestic ore, and 1.4% in richer foreign ore. Ore as

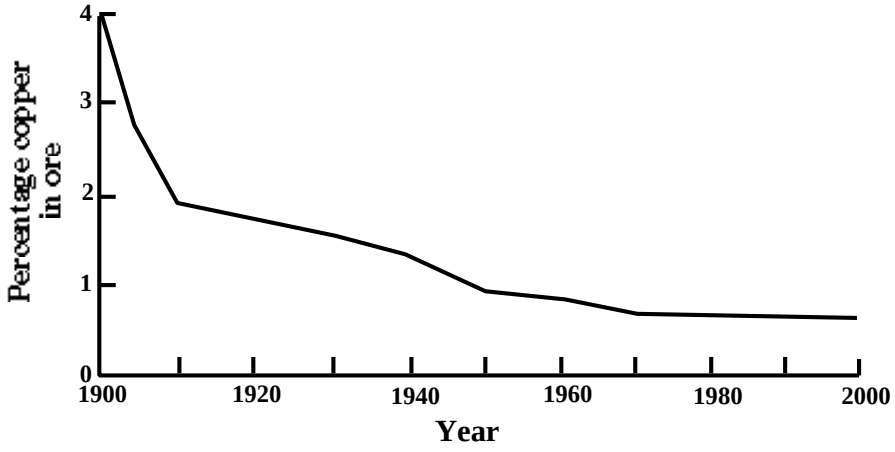


Figure 24.1 Average percentage of copper in ore that has been mined.

low as 0.1% copper may eventually be processed. Increased demand for a particular

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metal, coupled with the necessity to utilize lower grade ore, has a vicious multiplying effect upon the amount of ore that must be mined and processed, and accompanying environmental consequences.

The proper practice of industrial ecology can be used to significantly reduce the effects of mining and mining by-products. One way in which this can be done is to entirely eliminate the need for mining, utilizing alternate sources of materials. An example of such utilization, widely hypothesized but not yet put into practice to a large extent, is the extraction of aluminum from coal ash. This would have the double advantage of reducing amounts of waste ash and reducing the need to mine scarce aluminum ore.

24.4 METALS

The majority of elements are metals, most of which are of crucial importance as resources. The availability and annual usage of metals vary widely with the kind of metal. Some metals are abundant and widely used in structural applications; iron and aluminum are prime examples. Other metals, especially those of the platinum group (platinum, palladium, iridium, rhodium) are very precious and their use is confined to applications such as catalysts, filaments, or electrodes for which only small quantities are required. Some metals are considered to be "crucial" because of their applications for which no substitutes are available and shortages or uneven distribution in supply that occur. Such a metal is chromium, used to manufacture stainless steel (especially for parts exposed to high temperatures and corrosive gases), jet aircraft, automobiles, hospital equipment, and mining equipment. The platinum-group metals are used as catalysts in the chemical industry, in petroleum refining, and in automobile exhaust antipollution devices.

Metals exhibit a wide variety of properties and uses. They come from a number of different compounds; in some cases two or more compounds are significant mineral sources of the same metal. Usually these compounds are oxides or sulfides. However, other kinds of compounds and, in the cases of gold and platinum-group metals, the elemental (native) metals themselves serve as metal ore. Table 24.1 lists the important metals, their properties, major uses, and sources.

24.5 METAL RESOURCES AND INDUSTRIAL ECOLOGY

Considerations of industrial ecology are very important in extending and efficiently utilizing metal resources.[1] More than any other kind of resource, metals lend themselves to recycling and to the practice of industrial ecology. This section briefly addresses the industrial ecology of metals.

Aluminum

Aluminum metal has a remarkably wide range of uses resulting from its properties of low density, high strength, ready workability, corrosion resistance, and high electrical conductivity. Unlike some metals, such as toxic cadmium or lead, the use and disposal of aluminum presents no environmental problems. Further-more, it is one of the most readily recycled of all metals.

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Table 18.1. Worldwide and Domestic Metal Resources

Metals	Properties[a]	Major uses	Ore, aspects of resources[b]
Aluminum	mp 660°C, bp 2467°C, sg 2.70, malleable, ductile	Metal products, including autos, aircraft, electrical equipment. Conducts electricity better than copper per unit mass and is used in electrical transmission lines.	From bauxite ore containing 35-55% Al_2O_3. About 60 million metric tons of bauxite produced worldwide per year. U. S. resources of bauxite are 40 million metric tons, world resources about 15 billion metric tons.
Cadmium	Soft, ductile, silvery-white	Corrosion-resistant plating on steel and iron, alloys, bearings, pigments, rechargeable batteries.	Byproduct of zinc production, so annual production of cadmium parallels that of zinc. Abundant supply of toxic cadmium from this source has resulted in excessive dissipative uses.
Chromium	mp 1903°C, bp 2642°C, sg 7.14, hard, silvery color	Metal plating, stainless steel, wear-resistant and cutting tool alloys, chromium chemicals, including chromates.	From chromite, an oxide mineral containing Cr, Mg, Fe, Al. Resources of 1 billion metric tons in South Africa and Zimbabwe, large deposits in Russia, virtually none in the U.S.
Cobalt	mp 1495°C, bp 2880°C, sg 8.71, bright, silvery	Manufacture of hard, heat-resistant alloys, permanent magnet alloys, driers, pigments, animal feed additive.	From a variety of minerals, such as linnaeite, Co_3S_4, and as a by-product of other metals. Abundant global and U.S. resources.

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Table 18.1. (Cont.)

Copper	mp 1083°C, bp 2582°C, sg 8.96, ductile, malleable	Electrical conductors, alloys, chemicals. Many uses.	Occurs in low percentages as sulfides, oxides, and carbonates. U.S. consumption 1.5 million metric tons per year. World resources of 344 million metric tons, including 78 million in U.S.
Gold	mp 1063°C, bp 2660°C, sg 19.3	Jewelry, basis of currency, electronics, increasing industrial uses.	In various minerals at only around 10 ppm for ore currently processed in the U.S.; byproduct of copper refining. World resources of 1 billion oz., 80 million in U.S.
Iron	mp 1535°C, bp 2885°C, sg 7.86, silvery metal, in (rare) pure form	Most widely produced metal, usually as steel, a high-tensile-strength material containing 0.3-1.7% C. Made into many specialized alloys.	Occurs as hematite (Fe_2O_3), goethite ($Fe_2O_3 \cdot H_2O$), and magnetite (Fe_3O_4), abundant global and U.S. resources.
Lead	mp 327°C, bp 1750°C, sg 11.35, silvery color	Fifth most widely used metal, storage batteries, chemicals; uses in gasoline, pigments, and ammunition decreasing for environmental reasons.	Major source is galena, PbS. Worldwide consumption about 3.5 million metric tons, 1/3 in U.S. Global reserves about 140 million metric tons, 39 million metric tons U.S.
Manganese	mp 1244°C, bp 2040°C, sg 7.3, hard, brittle, gray-white	Sulfur and oxygen scavenger in steel, manufacture of alloys, dry cells, gasoline additive, chemicals	Found in several oxide minerals. About 20 million metric tons per year produced globally, 2 million consumed in U.S., no U.S. production, world reserves 6.5 billion metric tons.

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Table 18.1. (Cont.)

Mercury	mp -38°C, bp 357°C, sg 13.6, shiny, liquid metal	Instruments, electronic apparatus electrodes, chemicals.	From cinnabar, HgS. Annual world production 11,500 metric tons, 1/3 used in U.S. World resources 275,000 metric tons, 6,600 U.S.
Molybdenum	mp 2620°C, bp 4825°C, sg 9.01, ductile, silvery-gray	Alloys, pigments, catalysts, chemicals, lubricants.	Molybdenite (MoS_2) and wulfenite ($PbMoO_4$) are major kinds or ore. About 2/3global Mo production in U.S., large global resources.
Nickel	mp 1455°C, bp 2835°C, sg 8.90, silvery color	Alloys, coins, storage batteries, catalysts (such as for hydrogenation of vegetable oil).	Found in ore associated with iron. U.S. consumes 150,000 metric tons per year, 10% from domestic production, large domestic reserves of low-grade ore.
Platinum-group[c]	Resist chemical attack, perform well at high temperatures, good electrical properties, catalytic properties	Jewelry, alloys, catalysts, electrodes, filaments	In alluvial deposits produced by weathering and gravity separation. Most resources in Russia, South Africa, and Canada.
Silver	mp 961°C, bp 2193°C, sg 10.5, shiny metal	Photographic film, electronics, sterling ware, jewelry, bearings, dentistry.	Found with sulfide minerals, a by-product of Cu, Pb, Zn. Annual U.S. consumption of 150 million troy ounces, short supply.

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Table 18.1. (Cont.)

Tin	mp 232°C, bp 2687°C, sg 7.31	Coatings, solders, bearing alloys, bronze, chemicals, organo-metallic biocides.	Many forms associated with granitic rocks and chrysolites. Global consumption 190,000 metric tons/year, U.S. 60,000 metric tons/year, world resources 10 million metric tons.
Titanium	mp 1677°C, bp 3277°C, sg 4.5, silvery color	Strong, corrosion-resistant, used in aircraft, valves, pumps, paint pigments.	Commonly as TiO_2, ninth in elemental abundance, no shortages.
Tungsten	mp 3380°C, bp 5530°C, sg 19.3, gray	Very strong, high boiling point, used in alloys, tungsten carbide, drill bits, turbines, nuclear reactors.	Found as tungstates, such as scheelite ($CaWO_4$); U.S. has 7% world reserves, China 60%.
Vanadium	mp 1917°C, bp 3375°C, sg 5.87, gray	Used to make strong steel alloys.	In igneous rocks, primarily a by-product of other metals. U.S. consumption of 5,000 metric tons per year equals production.
Zinc	mp 420°C, bp 907°C, sg 7.14, bluish-white	Widely used in alloys (brass), galvanized steel, paint pigments, chemicals. Fourth in world metal production.	Found in many ore minerals. World production is 5 million metric tons per year, U.S. consumes 1.5 million metric tons per year. World resources 235 million metric tons, 20% in U.S.

[a] Abbreviations: mp, melting point; bp, boiling point; sg, specific gravity.

[b] All figures are approximate; quantities of minerals considered available depend upon price, technology, recent discoveries, and other factors, so that quantities quoted are subject to fluctuation.

[c] The platinum-group metals consist of platinum, palladium, iridium, ruthenium, and osmium, all of which are very valuable.

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The environmental problems associated with aluminum result from the mining and processing of aluminum ore. It occurs as a mineral called **bauxite**, which contains 40–60% alumina, Al_2O_3, associated with water molecules. Hydrated alumina is concentrated in bauxite, particularly in high-rainfall regions of the tropics, by the weathering away of more water-soluble constituents of soil (see laterites in Section 24.2). Bauxite ore is commonly strip mined from thin seams, so its mining causes significant disturbance to the geosphere. The commonly used Bayer process for aluminum refining dissolves alumina, shown below as the hydroxide $Al(OH)_3$, from bauxite at high temperatures with sodium hydroxide as sodium aluminate,

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O \quad (24.5.1)$$

leaving behind large quantities of caustic "red mud." This residue, which is rich in oxides of iron, silicon, and titanium, has virtually no uses and a high potential to produce pollution. Aluminum hydroxide is then precipitated in the pure form at lower temperatures and calcined at about 1200˚C to produce pure anhydrous Al_2O_3. The anhydrous alumina is then electrolyzed in molten cyrolite, Na_3AlF_6, at carbon electrodes to produce aluminum metal.

All aspects of aluminum production from bauxite are energy intensive. Large amounts of heat energy are required to heat the bauxite treated with caustic to extract sodium aluminate, and heat is required to calcine the hydrated alumina before it can be electrolyzed. Very large amounts of electrical energy are required to reduce aluminum to the metal in the electrolytic process for aluminum production.

An interesting possibility that could avoid many of the environmental problems associated with aluminum production is the use of coal fly ash as a source of the metal. Fly ash is produced in large quantities as a by-product of electricity generation, so it is essentially a free resource. As a raw material, coal fly ash is very attractive because it is anhydrous, thus avoiding the expense of removing water; it is finely divided, and it is homogeneous. Aluminum, along with iron, manganese, and titanium, can be extracted from coal fly ash with acid. If aluminum is extracted as the chloride salt, $AlCl_3$, it can be electrolyzed as the chloride by the ALCOA process. Although this process has not yet been proven to be competitive with the Bayer process, it may become so in the future.

Gallium is a metal that commonly occurs with aluminum ore and may be produced as a byproduct of aluminum manufacture. Gallium combined with arsenic or with indium and arsenic is useful in semiconductor applications, including integrated circuits, photoelectric devices, and lasers. Although important, these applications require only minuscule amounts of gallium compared with major metals.

Chromium

Chromium is of crucial importance because of its use in stainless steel and superalloys. These materials are vitally important to industrialized societies because of their applications in jet engines, nuclear power plants, chemical-resistant valves, and other applications in which a material that resists heat and chemical attack is required.

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As noted in Table 24.1, supplies of chromium are poorly distributed around the earth. It is important that chromium be handled according to good practices of industrial ecology. Several measures can be taken in this respect. Chromium is almost impossible to recover from chrome-plated objects, and this use should be eliminated insofar as possible, as has been done with much of the decorative chrome-plated adornments formerly put on automobiles. Chromium(VI) (chromate) is a toxic form of the metal and its uses should be eliminated wherever possible. The use of chromium in leather tanning and miscellaneous chemical applications should be curtailed. One important use of chromium is in the preparation of treated CCA lumber, which resists fungal decay and termites. The widespread use of this lumber has greatly extended the life of wood products, which is in keeping with the practice of industrial ecology. However, its use of toxic arsenic, scarce copper, and even more scarce chromium are negatives, and alternative means of preserving lumber still need to be found.

Copper

Copper is a low-toxicity, corrosion-resistant metal widely used because of its workability (ductility and malleability), electrical conductivity, and ability to conduct heat. In addition to its use in electrical wire, where in some applications it is now challenged by aluminum, copper is also used in tubing, copper pipe, shims, gaskets, and other applications.

There are at least two major environmental problems associated with the extraction and refining of copper. The first of these is the dilute form in which copper ore now occurs (see Figure 24.1), such that in the U.S. 150–175 tons of inert material (not counting overburden removed in strip mining) must be processed and discarded to produce a ton of copper metal. The second problem is the occurrence of copper as the sulfide so that in the production of copper, large amounts of sulfur must be recovered as a by-product or, unfortunately in some less developed countries, released into the atmosphere as pollutant SO_2.

An advantage to copper for recycling is that it is used primarily as the metal, which represents "stored energy" in that it does not require energy for reduction to the metal. Recycling rates of scrap copper appear low in part because so much of the inventory of copper metal is tied up in long-lasting electrical wire, in structures, and other places where the lifetime of the metal is long. (This is in contrast to lead, where the main source of recycled metal is storage batteries, which last only 2–4 years.) An impediment to copper recycling is the difficulty of recovering copper components from circuits, plumbing, and other applications.

Cobalt

Cobalt is a "strategic" metal with very important applications in alloys, particularly in heat-resistant applications, such as jet engines. The major source of cobalt is as a byproduct of copper refining, although it can also be obtained as a byproduct of nickel and lead. As much as 50% of the cobalt in these sources is lost to tailings, slag, or other wastes, so there is a significant potential to improve the recovery of cobalt. Relatively low percentages of cobalt are recycled as scrap.

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Lead

The industrial ecology of lead is very important because of the widespread use of this metal and its toxicity. Global fluxes of lead from the anthrosphere are shown in Figure 24.2.

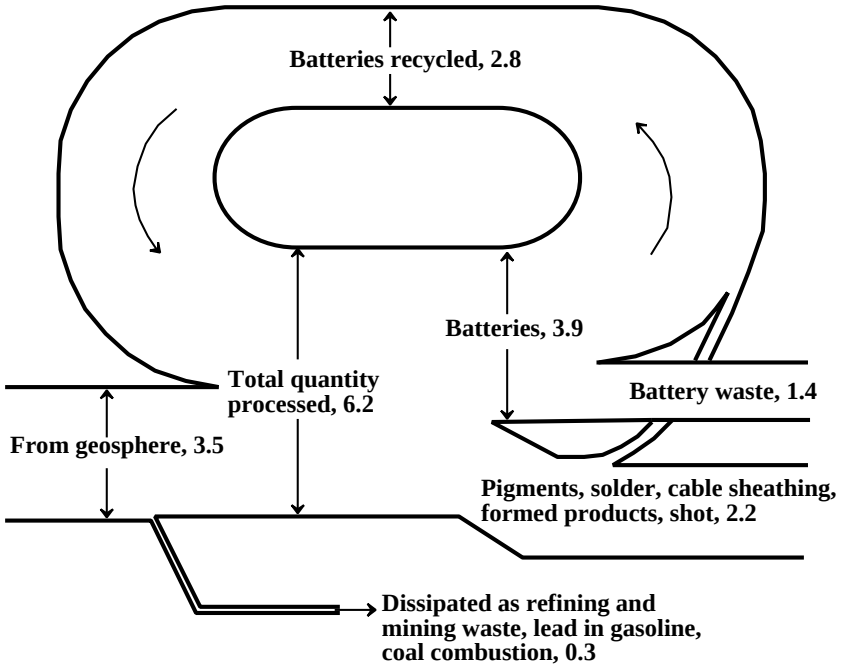


Figure 24.2 Flux of lead in the anthrosphere, globally, on an annual basis in millions of tons per year. Lead from the geosphere includes metal mined and a small quantity dissipated by coal combustion.

Somewhat more than half of the lead processed by humans comes from the geosphere, mostly as lead mined for the metal, and with a very small fraction contained in coal that is burned. By far the greatest use of lead is in batteries, and the amount of battery lead recycled each year approaches that taken from the geosphere. A small fraction of lead is dissipated as wastes associated with the mining and refining of the metal and as lead in gasoline, an amount that is decreasing as use of unleaded gasoline becomes prevalent around the world. A significant quantity of lead goes into various uses other than batteries, including pigments, solder, cable sheathing, formed products, and shot in ammunition. Only a small fraction of lead from these uses is recycled, and this represents a potential improvement in the conservation of lead. Another area in which improvements can be made is to eliminate or greatly reduce nonbattery uses of lead, as has been done in the case of lead shot and pigments. Although a large fraction of lead in batteries is recycled, about 1/3 of the lead used in batteries is lost; this represents another area of potential improvement in the utilization of lead.

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Zinc

Zinc is relatively abundant and not particularly toxic, so its industrial ecology is of less concern than that of toxic lead or scarce chromium. As with other metals, the mining and processing of zinc can pose some environmental concerns. Zinc occurs as ZnS (a mineral called sphalerite), and the sulfur must be reclaimed in the smelting of zinc. Zinc minerals often contain significant fractions of lead and copper, as well as significant amounts of toxic arsenic and cadmium.

Zinc is widely used as the metal, and lesser amounts are used to make zinc chemicals. One of the larger uses for zinc is as a corrosion-resistant coating on steel. This application, refined to a high degree in the automotive industry in recent years, has significantly lengthened the life span of automotive bodies and frames. It is difficult to reclaim zinc from zinc plating. However, zinc is a volatile element and it can be recovered in baghouse dust from electric arc furnaces used to reprocess scrap steel.

Zinc is used along with copper to make the alloy called brass. Brass is very well adapted to the production of various parts and objectives. It is recyclable, and significant quantities of brass are recycled as wastes from casting, machining, and as postconsumer waste.

Although a number of zinc compounds are synthesized and used, by far the most important of them is zinc oxide, ZnO. Formerly widely used as a paint pigment, this white substance is now employed as an accelerating and activating agent for hardening rubber products, particularly tires. Tire wear is a major vector for the transfer of zinc to the environment and, since it occurs with zinc, toxic cadmium is also dissipated to the environment by tire wear. The other two major compounds of zinc employed commercially are zinc chloride used in dry cells, as a disinfectant, and to vulcanize rubber, and zinc sulfide, used in zinc electroplating baths and to manufacture zinc-containing insecticides, particularly Zineb.®

Two aspects of zinc can be addressed in respect to its industrial ecology. The first of these is that, although it is not very toxic to animals, zinc is phytotoxic (toxic to plants) and soil can be "poisoned" by exposure to zinc from zinc smelting or from application of zinc-rich sewage sludge. The second of these is that the recycling of zinc is complicated by its dispersal as a plating on other metals. However, means do exist to reclaim significant fractions of such zinc, such as from electric arc furnaces as mentioned above.

Potassium

Potassium deserves special mention as a metal because the potassium ion, K^+, is an essential element required for plant growth. It is mined as potassium minerals and applied to soil as plant fertilizer. Potassium minerals consist of potassium salts, generally KCl. Such salts are found as deposits in the ground or may be obtained from some brines. Very large deposits are found in Saskatchewan, Canada. These salts are all quite soluble in water.

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24.6 NONMETAL MINERAL RESOURCES

A number of minerals other than those used to produce metals are important resources. There are so many of these that it is impossible to discuss them all in this chapter; however, mention will be made of the major ones. As with metals, the environmental aspects of mining many of these minerals are quite important. Typically, even the extraction of ordinary rock and gravel can have important environmental effects.

Clays are secondary minerals formed by weathering processes on parent minerals (see Chapter 15, Section 15.7). Clays have a variety of uses. About 70% of the clays used are miscellaneous clays of variable composition that have uses for a number of applications including filler (such as in paper), brick manufacture, tile manufacture, and Portland cement production. Somewhat more than 10% of the clay used is fireclay, which has the characteristic of being able to withstand firing at high temperatures without warping. This clay is used to make a variety of refractories, pottery, sewer pipe, tile, and brick. Somewhat less than 10% of the clay that is used is kaolin, which has the general formula $Al_2(OH)_4Si_2O_5$. Kaolin is a white mineral that can be fired without losing shape or color. It is employed to make paper filler, refractories, pottery, dinnerware, and as a petroleum-cracking catalyst. About 7% of clay mined consists of bentonite and fuller's earth, a clay of variable composition used to make drilling muds, petroleum catalyst, carriers for pesticides, sealers, and clarifying oils. Very small quantities of a highly plastic clay called ball clay are used to make refractories, tile, and whiteware. U.S. production of clay is about 60 million metric tons per year, and global and domestic resources are abundant.

Fluorine compounds are widely used in industry. Large quantities of fluorspar, CaF_2, are required as a flux in steel manufacture. Synthetic and natural cryolite, Na_3AlF_6, is used as a solvent for aluminum oxide in the electrolytic preparation of aluminum metal. Sodium fluoride is added to water to help prevent tooth decay, a measure commonly called water fluoridation. World reserves of high-grade fluorspar are around 190 million metric tons, about 13% of which is in the United States. This is sufficient for several decades at projected rates of use. A great deal of by-product fluorine is recovered from the processing of fluorapatite, $Ca_5(PO_4)_3F$, used as a source of phosphorus (see below).

Micas are complex aluminum silicate minerals that are transparent, tough, flexible, and elastic. Muscovite, $K_2O{\cdot}3Al_2O_3{\cdot}6\ SiO_2{\cdot}2H_2O$, is a major type of mica. Better grades of mica are cut into sheets and used in electronic apparatus, capacitors, generators, transformers, and motors. Finely divided mica is widely used in roofing, paint, welding rods, and many other applications. Sheet mica is imported into the United States, and finely divided "scrap" mica is recycled domestically. Shortages of this mineral are unlikely.

Pigments and **fillers** of various kinds are used in large quantities. The only naturally occurring pigments still in wide use are those containing iron. These minerals are colored by limonite, an amorphous brown-yellow compound with the formula $2Fe_2O_3{\cdot}3H_2O$, and hematite, composed of gray-black Fe_2O_3. Along with varying quantities of clay and manganese oxides, these compounds are found in ocher, sienna, and umber. Manufactured pigments include carbon black, titanium dioxide, and zinc pigments. About 1.5 million metric tons of carbon black, manufactured by the partial

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combustion of natural gas, are used in the U.S. each year, primarily as a reinforcing agent in tire rubber.

Over 7 million metric tons of minerals are used in the U.S. each year as fillers for paper, rubber, roofing, battery boxes, and many other products. Among the minerals used as fillers are carbon black, diatomite, barite, fuller's earth, kaolin (see clays, above), mica, limestone, pyrophyllite, and wollastonite ($CaSiO_3$).

Although **sand** and **gravel** are the cheapest of mineral commodities per ton, the average annual dollar value of these materials is greater than all but a few mineral products because of the huge quantities involved. In tonnage, sand and gravel production is by far the greatest of nonfuel minerals. Almost 1 billion tons of sand and gravel are employed in construction in the U.S. each year, largely to make concrete structures, road paving, and dams. Slightly more than that amount is used to manufacture Portland cement and as construction fill. Although ordinary sand is predominantly silica, SiO_2, about 30 million tons of a purer grade of silica are consumed in the U.S. each year to make glass, high-purity silica, silicon semiconductors, and abrasives.

At present, old river channels and glacial deposits are used as sources of sand and gravel. Many valuable deposits of sand and gravel are covered by construction and lost to development. Transportation and distance from source to use are especially crucial for this resource. Environmental problems involved with defacing land can be severe, although bodies of water used for fishing and other recreational activities frequently are formed by removal of sand and gravel.

24.7 PHOSPHATES

Phosphate minerals are of particular importance because of their essential use in the manufacture of fertilizers applied to land to increase crop productivity. In addition, phosphorus is used for supplementation of animal feeds, synthesis of detergent builders, and preparation of chemicals such as pesticides and medicines. The most common phosphate minerals are hydroxyapatite, $Ca_5(PO_4)_3(OH)$, and fluorapatite, $Ca_5(PO_4)_3F$. Ions of Na, Sr, Th, and U are found substituted for calcium in apatite minerals. Small amounts of PO_4^{3-} can be replaced by AsO_4^{3-} and the arsenic must be removed for food applications. Approximately 17% of world phosphate production is from igneous minerals, primarily fluorapatites. About three-fourths of world phosphate production is from sedimentary deposits, generally of marine origin. Vast deposits of phosphate, accounting for approximately 5% of world phosphate production, are derived from guano droppings of seabirds and bats. Current U.S. production of phosphate rock is around 40 million metric tons per year, most of it from Florida. Idaho, Montana, Utah, Wyoming, North Carolina, South Carolina, and Tennessee also have sources of phosphate. Reserves of phosphate minerals in the United States amount to 10.5 billion metric tons, containing approximately 1.4 billion metric tons of phosphorus.

Phosphate in the naturally occurring minerals is not sufficiently available to be used as fertilizer. For commercial phosphate fertilizer production, these minerals are treated with phosphoric or sulfuric acids to produce more soluble superphosphates.

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$$2Ca_5(PO_4)_3F(s) + 14H_3PO_4 + 10H_2O \rightarrow 2HF(g) + 10Ca(H_2PO_4)_2 \cdot H_2O \quad (24.7.1)$$

$$2Ca_5(PO_4)_3F(s) + 7H_2SO_4 + 3H_2O \rightarrow 2HF(g) + 3Ca(H_2PO_4)_2 \cdot H_2O + 7CaSO_4 \quad (24.7.2)$$

The HF produced as a byproduct of superphosphate production can create air pollution problems, and the recovery of fluorides is an important aspect of the industrial ecology of phosphate production.

Phosphate minerals are rich in trace elements required for plant growth, such as boron, copper, manganese, molybdenum, and zinc. Ironically, these elements are lost in processing phosphate for fertilizers and are sometimes added later.

Ammonium phosphates are excellent, highly soluble phosphate fertilizers. Liquid ammonium polyphosphate fertilizers consisting of ammonium salts of pyrophosphate, triphosphate, and small quantities of higher polymeric phosphate anions in aqueous solution can be used as phosphate fertilizers. The polyphosphates are believed to have the additional advantage of chelating iron and other micronutrient metal ions, thus making the metals more available to plants.

There are at least two major reasons that the industrial ecology of phosphorus is particularly important. The first of these is that current rates of phosphate use would exhaust known reserves of phosphate within two or three generations. Although additional sources of phosphorus will be found and exploited, it is clear that this essential mineral is in distressingly short supply relative to human consumption; phosphate shortages, along with sharply higher prices, will eventually cause a crisis in food production. The second significant aspect of the industrial ecology of phosphorus is the pollution of waterways by waste phosphate, a plant and algal nutrient. This results in excessive growth of algae in the water, followed by decay of the plant biomass, consumption of dissolved oxygen, and an undesirable condition of eutrophication.

Excessive use of phosphate coupled with phosphate pollution suggests that phosphate wastes, such as from sewage treatment, should be substituted as sources of plant fertilizer. Several other partial solutions to the problem of phosphate shortages are the following:

- Development and implementation of methods of fertilizer application that maximize efficient utilization of phosphate
- Genetic engineering of plants that have minimal phosphate requirements and that utilize phosphorus with maximum efficiency
- Development of systems to maximize the utilization of phosphorus-rich animal wastes

24.8 SULFUR

Sulfur is an important nonmetal; its greatest single use is in the manufacture of sulfuric acid. However, the element is employed in a wide variety of other industrial and agricultural products. Current consumption of sulfur amounts to approximately

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10 million metric tons per year in the United States. The four most important sources of sulfur are (in decreasing order) deposits of elemental sulfur, H_2S recovered from sour natural gas, organic sulfur recovered from petroleum, and pyrite (FeS_2). Recovery of sulfur from coal used as a fuel is a huge potential, largely untapped, source of this important nonmetal.

The resource situation for sulfur differs from that of phosphorus in several significant respects. Although sulfur is an essential nutrient like phosphorus, most soils contain sufficient amounts of nutrient sulfur, and the major uses of sulfur are in the industrial sector. The sources of sulfur are varied and abundant and supply is no problem either in the United States or worldwide; sulfur recovery from fossil fuels as a pollution control measure could even result in surpluses of this element.

About 90% of the use of sulfur in the world is for the manufacture of sulfuric acid. Almost 2/3 of the sulfuric acid consumed is used to make phosphate fertilizers as discussed in Section 24.7, in which case, the phosphorus ends up as waste "phospho-gypsum," $CaSO_4 \cdot xH_2O$. Other uses of sulfur include lead storage batteries, steel pickling, petroleum refining, extraction of copper from copper ore, and the chemical industry.

The industrial ecology of sulfur needs to emphasize reduction of wastes and sulfur pollution, rather than supply of this element. Unlike many resources, such as most common metals, the uses of sulfur are for the most part dissipative, and the sulfur is "lost" to agricultural land, paper products, petroleum products, or other environmental sinks. There are two major environmental concerns with sulfur. One of these is the emission of sulfur into the atmosphere, which occurs mostly as pollutant sulfur dioxide and is largely manifested by production of acidic precipitation and dry deposition. The second major environmental concern with sulfur is that it is used mostly as sulfuric acid and is not incorporated into products, thus posing the potential to pollute water and create acidic wastes. Acid purification units are available to remove significant amounts of sulfuric acid from waste acid solutions for recycling.

Gypsum

Calcium sulfate in the form of the dihydrate $CaSO_4 \cdot 2H_2O$ is the mineral **gypsum**, one of the most common forms in which waste sulfur is produced. As noted, large quantities of this material are produced as a by-product of phosphate fertilizer manufacture. Another major source of gypsum is its production when lime is used to remove sulfur dioxide from power plant stack gas,

$$Ca(OH)_2 + SO_2 \rightarrow CaSO_3 + H_2O \qquad (24.8.1)$$

to produce a calcium sulfite product that can be oxidized to calcium sulfate. About 100 million metric tons of gypsum are mined each year for a variety of uses, including production of Portland cement, to produce wallboard, as a soil conditioner to loosen tight clay soils, and numerous other applications.

Calcium sulfate from industrial or natural (gypsum) sources can be calcined at a very low temperature of only 159°C to produce $CaSO_4 \cdot {}^1/_2H_2O$, a material known as plaster of Paris, which was once commonly used for the manual application of plaster to walls. Plaster of Paris mixed with water forms a plastic material that sets up as the

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solid dihydrate,

$$CaSO_4 \cdot {}^1/_2H_2O + {}^3/_2H_2O \rightarrow CaSO_4 \cdot 2H_2O \quad (24.8.2)$$

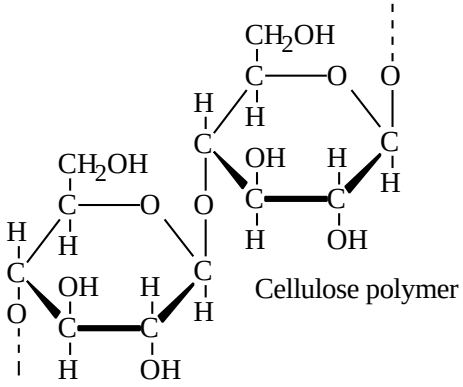
Cast into sheets coated with paper, this material produces plasterboard commonly used for the interior walls of homes and other buildings. Historically, plaster of Paris was used for mortar and other structural applications, and it has the potential for similar applications today.

The very large quantities of gypsum that are mined suggest that by-product calcium sulfate, especially that produced with phosphate fertilizers and from flue gas desulfurization, should be a good candidate for reclamation through the practice of industrial ecology. The low temperature (see above) required to convert hydrated calcium sulfate to $CaSO_4 \cdot {}^1/_2H_2O$, which can be set up as a solid by mixing with water, suggests that the energy requirements for a gypsum-based by-products industry should be modest. Low-density gypsum blown as a foam and used as a filler in composites along with sturdy reinforcing materials should have good insulating, fire-resistant, and structural properties for building construction.

24.9 WOOD—A MAJOR RENEWABLE RESOURCE

Fortunately, one of the major natural resources in the world, wood, is a renewable resource. Production of wood and wood products is the fifth largest industry in the United States, and forests cover one-third of the United States surface area. Wood ranks first worldwide as a raw material for the manufacture of other products, including lumber, plywood, particle board, cellophane, rayon, paper, methanol, plastics, and turpentine.

Chemically, wood is a complicated substance consisting of long cells having thick walls composed of polysaccharides such as cellulose,



Cellulose polymer

The polysaccharides in cell walls account for approximately three-fourths of *solid wood*, wood from which extractable materials have been removed by an alcohol-benzene mixture. Wood typically contains a few tenths of a percent of ash (mineral residue left from the combustion of wood).

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A wide variety of organic compounds can be extracted from wood by water, alcohol-benzene, ether, and steam distillation. These compounds include tannins, pigments, sugars, starch, cyclitols, gums, mucilages, pectins, galactans, terpenes, hydrocarbons, acids, esters, fats, fatty acids, aldehydes, resins, sterols, and waxes. Substantial amounts of methanol (sometimes called *wood alcohol*) are obtained from wood, particularly when it is pyrolyzed. Methanol, once a major source of liquid fuel, is now being used to a limited extent as an ingredient of some gasoline blends (see gasohol in Section 24.19).

A major use of wood is in paper manufacture. The widespread use of paper is a mark of an industrialized society. The manufacture of paper is a highly advanced technology. Paper consists essentially of cellulosic fibers tightly pressed together. The lignin fraction must first be removed from the wood, leaving the cellulosic fraction. Both the sulfite and alkaline processes for accomplishing this separation have resulted in severe water and air pollution problems, now significantly alleviated through the application of advanced treatment technologies.

Wood fibers and particles can be used for making fiberboard, paper-base laminates (layers of paper held together by a resin and formed into the desired structures at high temperatures and pressures), particle board (consisting of wood particles bonded together by a phenol-formaldehyde or urea-formaldehyde resin), and nonwoven textile substitutes made of wood fibers bonded by adhesives. Chemical processing of wood enables the manufacture of many useful products, including methanol and sugar. Both of these substances are potential major products from the 60 million metric tons of wood wastes produced in the U.S. each year.

24.10 THE ENERGY PROBLEM

Since the 1973–74 "energy crisis," much has been said and written, many learned predictions have gone awry, and some concrete action has even taken place. Catastrophic economic disruption, people "freezing in the dark," and freeways given over to bicycles (perhaps a good idea) have not occurred. Nevertheless, uncertainties over petroleum availability and price, along with market disruptions, such as the painfully increased gasoline, diesel fuel, and heating oil prices in 2000, have caused energy to be one of the major problems of modern times.

In the U.S., concern over energy supplies and measures taken to ensure alternate supplies reached a peak in the late 1970s. Significant programs on applied energy research were undertaken in the areas of renewable energy sources, efficiency, and fossil fuels. The financing of these efforts reached a peak around 1980, then dwindled significantly after that date. By 1999, an abundance of fossil energy had resulted in a false sense of security regarding energy sources.

The solutions to energy problems are strongly tied to environmental considerations. For example, a massive shift of the energy base to coal in nations that now rely largely on petroleum for energy would involve much more strip mining, potential production of acid mine water, use of scrubbers, and release of greenhouse gases (carbon dioxide from coal combustion and methane from coal mining). Similar examples could be cited for most other energy alternatives.

Dealing with the energy problem requires a heavy reliance on technology, which is discussed in numerous places in this book. Computerized control of transportation

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and manufacturing processes enables much more efficient utilization of energy. New and improved materials enable higher peak temperatures and therefore greater extraction of usable energy in thermal energy conversion processes. Innovative manufacturing processes have greatly lowered the costs of photovoltaic cells used to convert sunlight directly to energy.

24.11 WORLD ENERGY RESOURCES

At present, most of the energy consumed by humans is produced from fossil fuels. Estimates of the amounts of fossil fuels available differ; those of the quantities of recoverable fossil fuels in the world before 1800 are given in Figure 24.3. By far the greatest recoverable fossil fuel is in the form of coal and lignite. Furthermore, only a small percentage of this energy source has been utilized to date, whereas much of the recoverable petroleum and natural gas has already been consumed. Projected use of these latter resources indicates rapid depletion.

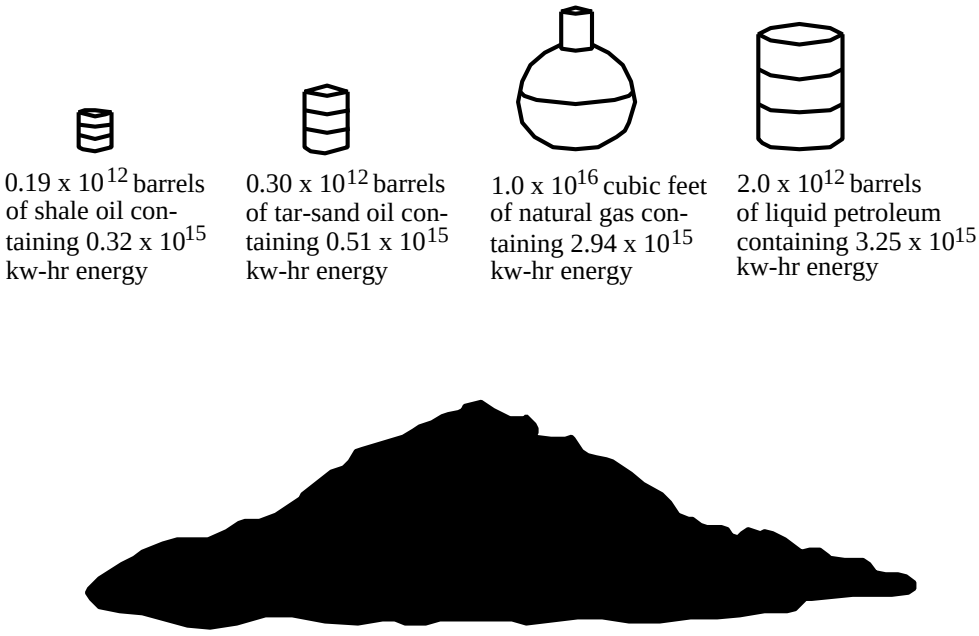


Figure 24.3 Original amounts of the world's recoverable fossil fuels (quantities in thermal kilowatt hours of energy based upon data taken from M. K. Hubbert, "The Energy Resources of the Earth," in *Energy and Power*, W. H. Freeman and Co., San Francisco, 1971).

Although world coal resources are enormous and potentially can fill energy needs for a century or two, their utilization is limited by environmental disruption from mining and emissions of carbon dioxide and sulfur dioxide. These would become intolerable long before coal resources were exhausted. Assuming only uranium-235 as a fission fuel source, total recoverable reserves of nuclear fuel are roughly about the same as fossil fuel reserves. These are many orders of magnitude higher if the use of breeder reactors is assumed. Extraction of only 2% of the deuterium present in the

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earth's oceans would yield about a billion times as much energy by controlled nuclear fusion as was originally present in fossil fuels, a prospect tempered by the lack of success in developing a controlled nuclear fusion reactor. Geothermal power, currently utilized in northern California, Italy, and New Zealand, has the potential for providing a significant percentage of energy worldwide. The same limited potential is characteristic of several renewable energy resources, including hydroelectric energy, tidal energy, and especially wind power. All of these will continue to contribute significant, but relatively small, amounts of energy. Renewable, nonpolluting solar energy comes as close to being an ideal energy source as any available. It almost certainly has a bright future.

24.12 ENERGY CONSERVATION

Any consideration of energy needs and production must take energy conservation into consideration. This does not have to mean cold classrooms with thermostats set at 60˚F in mid-winter, nor swelteringly hot homes with no air-conditioning, nor total reliance on the bicycle for transportation, although these and even more severe conditions are routine in many countries. The fact remains that the United States has wasted energy at a deplorable rate. Often with funds gained from the artificial wealth of an inflated stock market, many U.S. citizens purchased huge, highly uneconomical "sport utility vehicles" in the 1990s. U.S. energy consumption is higher per capita than that of some other countries that have equal, or significantly better, living standards. Obviously, a great deal of potential exists for energy conservation that will ease the energy problem.

Transportation is the economic sector with the greatest potential for increased efficiencies. The private auto and airplane are only about one-third as efficient as buses or trains, and shipping freight by truck requires about 3800 Btu/ton-mile, compared with only 670 Btu/ton-mile for a train. Compared to rail, truck transport is inefficient, dangerous, labor-intensive, and environmentally disruptive. Major shifts in current modes of transportation in the U.S. will not come without anguish, but energy conservation dictates that they be made.

Household and commercial uses of energy are relatively efficient. Here again, appreciable savings can be made. The all-electric home requires much more energy (considering the percentage wasted in generating electricity) than a home heated with fossil fuels. The sprawling ranch-house-style home uses much more energy per person than does an apartment unit or row house. Improved insulation, sealing around the windows, and other measures can conserve a great deal of energy. Electric generating plants centrally located in cities can provide waste heat for commercial and residential heating and cooling and, with proper pollution control, can use municipal refuse for part of their fuel, thus reducing quantities of solid wastes requiring disposal. As scientists and engineers undertake the crucial task of developing alternative energy sources to replace dwindling petroleum and natural gas supplies, energy conservation must receive proper emphasis. In fact, zero energy-use growth, at least on a per capita basis, is a worthwhile and achievable goal. Such a policy would go a long way toward solving many environmental problems. With ingenuity, planning, and proper management, it could be achieved while increasing the standard of living and quality of life.

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24.13 ENERGY CONVERSION PROCESSES

As shown in Figure 24.4, energy occurs in several forms and must be converted to other forms. The efficiencies of conversion vary over a wide range. Conversion of electrical energy to radiant energy by incandescent light bulbs is very inefficient—less than 5% of the energy is converted to visible light and the remainder is wasted as heat. At the other end of the scale, a large electrical generator is around 80% efficient in producing electrical energy from mechanical energy. The once much-publicized Wankel rotary engine converts chemical to mechanical energy with an efficiency of about 18%, compared with 25% for a gasoline-powered piston engine and about 37% for a diesel engine. A modern coal-fired steam-generating power plant converts chemical energy to electrical energy with an overall efficiency of about 40%.

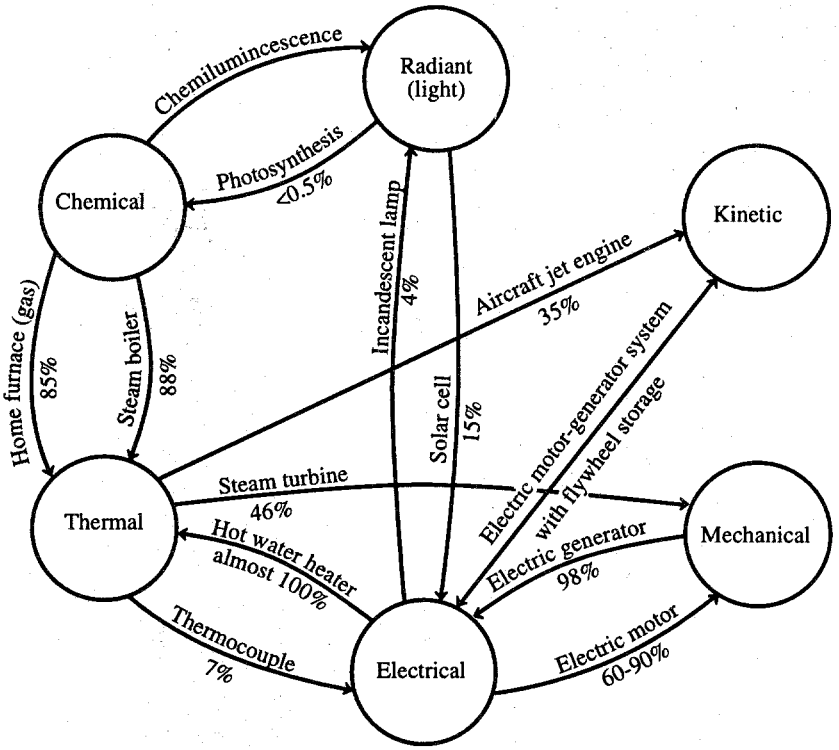


Figure 24.4 Kinds of energy and examples of conversion between them, with conversion efficiency percentages.

One of the most significant energy conversion processes is that of thermal energy to mechanical energy in a heat engine such as a steam turbine. The Carnot equation,

$$\text{Percent efficiency} = \frac{T_1 - T_2}{T_1} \times 100 \qquad (24.13.1)$$

states that the percent efficiency is given by a fraction involving the inlet temperature (for example, of steam), T_1, and the outlet temperature, T_2. These temperatures are

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expressed in Kelvin (˚C + 273). Typically, a steam turbine engine operates with approximately 810 K inlet temperature and 330 K outlet temperature. These temperatures substituted into the Carnot equation give a maximum theoretical efficiency of 59%. However, because it is not possible to maintain the incoming steam at the maximum temperature and because mechanical energy losses occur, overall efficiency of conversion of thermal energy to mechanical energy in a modern steam power plant is approximately 47%. Taking into account losses from conversion of chemical to thermal energy in the boiler, the total efficiency is about 40%.

Some of the greatest efficiency advances in the conversion of chemical to mechanical or electrical energy have been made by increasing the peak inlet temperature in heat engines. The use of superheated steam has raised T_1 in a steam power plant from around 550 K in 1900 to about 850 K at present. Improved materials and engineering design, therefore, have resulted in large energy savings.

The efficiency of nuclear power plants is limited by the maximum temperatures attainable. Reactor cores would be damaged by the high temperatures used in fossil-fuel-fired boilers and have a maximum temperature of approximately 620 K. Because of this limitation, the overall efficiency of conversion of nuclear energy to electricity is about 30%.

Most of the 60% of energy from fossil-fuel-fired power plants and 70% of energy from nuclear power plants that is not converted to electricity is dissipated as heat, either into the atmosphere or into bodies of water and streams. The latter is thermal pollution, which may either harm aquatic life or, in some cases, actually increase bioactivity in the water to the benefit of some species. This waste heat is potentially very useful in applications like home heating, water desalination, and aquaculture (growth of plants in water).

Some devices for the conversion of energy are shown in Figure 24.5. Substantial advances have been made in energy conversion technology over many decades and more can be projected for the future. The use of higher temperatures and larger generating units have increased the overall efficiency of fossil-fueled electrical power generation from less than 4% in 1900 to more than 40%. An approximately four fold increase in the energy-use efficiency of rail transport occurred during the 1940s and 1950s with the replacement of steam locomotives with diesel locomotives. During the coming decades, increased efficiency can be anticipated from such techniques as combined power cycles in connection with generation of electricity. Magnetohydrodynamics (Figure 24.7) may be developed as a very efficient energy source used in combination with conventional steam generation. Entirely new devices such as thermonuclear reactors for the direct conversion of nuclear fusion energy to electricity will possibly be developed.

24.14 PETROLEUM AND NATURAL GAS

Since its first commercial oil well in 1859, the United States has produced somewhat more than 100 billion barrels of oil, most of it in recent years. In 1994, world petroleum consumption was at a rate of about 65 million barrels per day.

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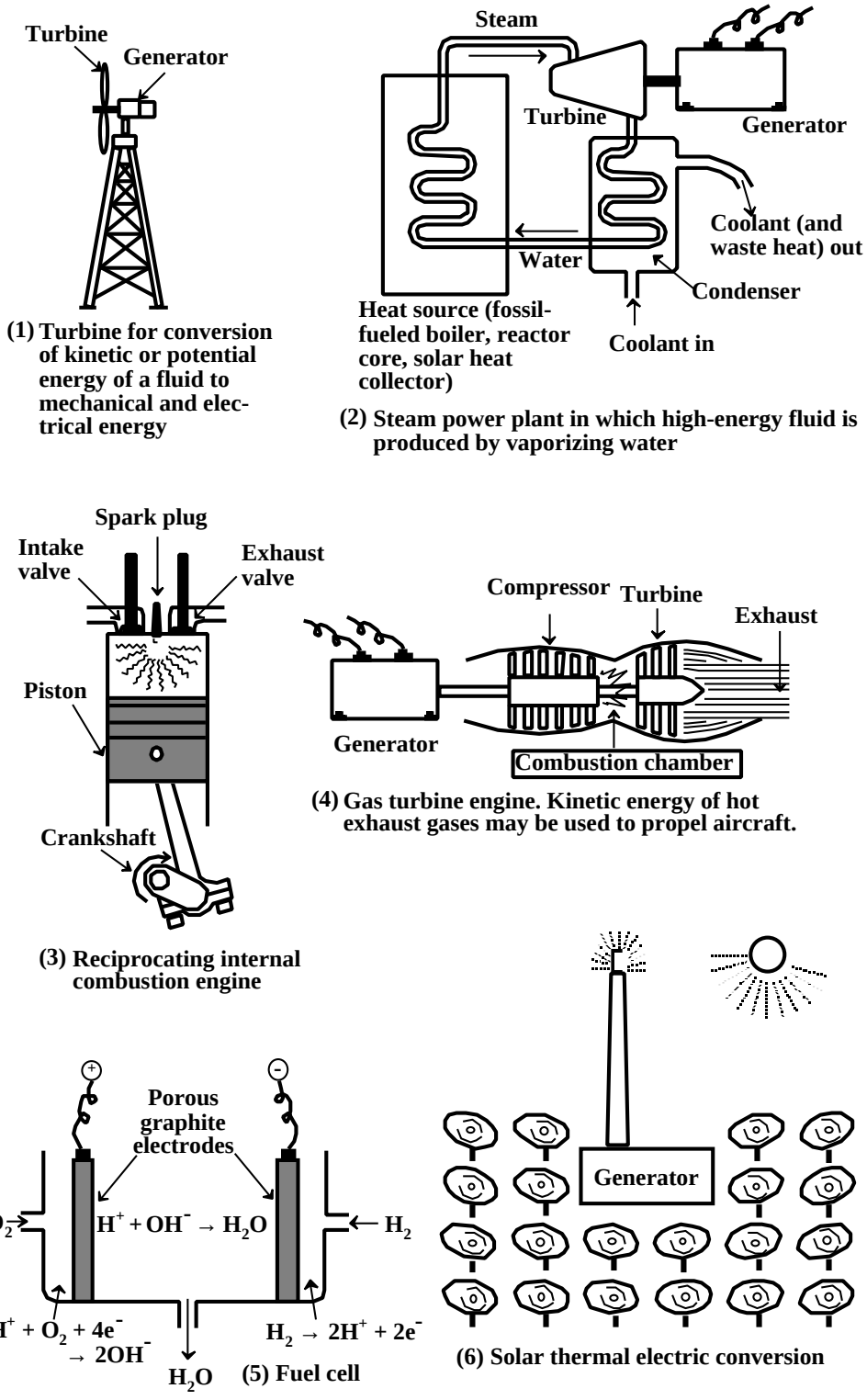


Figure 24.5 Some energy conversion devices.

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Liquid petroleum is found in rock formations ranging in porosity from 10 to 30%. Up to half of the pore space is occupied by water. The oil in these formations must flow over long distances to an approximately 15-cm-diameter well from which it is pumped. The rate of flow depends on the permeability of the rock formation, the viscosity of the oil, the driving pressure behind the oil, and other factors. Because of limitations in these factors, **primary recovery** of oil yields an average of about 30% of the oil in the formation, although it is sometimes as little as 15%. More oil can be obtained using **secondary recovery** techniques, which involve forcing water under pressure into the oil-bearing formation to drive the oil out. Primary and secondary recovery together typically extract somewhat less than 50% of the oil from a formation. Finally, **tertiary recovery** can be used to extract even more oil, normally through the injection of pressurized carbon dioxide, which forms a mobile solution with the oil and allows it to flow more easily to the well. Other chemicals, such as detergents, may be used to aid in tertiary recovery. Currently, about 300 billion barrels of U.S. oil are not available through primary recovery alone. A recovery efficiency of 60% through secondary or tertiary techniques could double the amount of available petroleum. Much of this would come from fields that have already been abandoned or essentially exhausted using primary recovery techniques.

Shale oil is a possible substitute for liquid petroleum. Shale oil is a pyrolysis product of oil shale, a rock containing organic carbon in a complex structure of biological origin from eons past called kerogen. Oil shale is believed to contain approximately 1.8. trillion barrels of shale oil that could be recovered from deposits in Colorado, Wyoming, and Utah. In the Colorado Piceance Creek basin alone, more than 100 billion barrels of oil could be recovered from prime shale deposits.

Shale oil can be recovered from the parent mineral by retorting the mined shale in a surface retort. A major environmental disadvantage is that this process requires the mining of enormous quantities of mineral and disposal of the spent shale, which has a volume greater than the original mineral. *In situ* retorting limits the control available over infiltration of underground water and resulting water pollution. Water passing through spent shale becomes quite saline, so there is major potential for saltwater pollution.

During the late 1970s and early 1980s, several corporations began building facilities for shale oil extraction in northwestern Colorado. Large investments were made in these operations, and huge expenditures were projected for commercialization. Falling crude oil prices caused all these operations to be canceled. A large project for the recovery of oil from oil sands in Alberta, Canada, was also canceled in the 1980s.

Natural gas, consisting almost entirely of methane, has become more attractive as an energy source, with recent discoveries and development of substantial new sources of this premium fuel. In addition to its use as a fuel, natural gas can be converted to many other hydrocarbon materials. It can be used as a raw material for the Fischer-Tropsch synthesis of gasoline. New unconventional sources of natural gas, such as may exist in geopressurized zones, could provide abundant energy reserves for the U.S., though at substantially increased prices.

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24.15 COAL

From Civil War times until World War II, coal was the dominant energy source behind industrial expansion in most nations. However, after World War II, the greater convenience of lower-cost petroleum resulted in a decrease in the use of coal for energy in the U.S. and in a number of other countries. Annual coal production in the U.S. fell by about one-third, reaching a low of approximately 400 million tons in 1958. Since that time U.S. production has increased. Several statistics illustrate the importance of coal as a source of energy by earth's population. Overall, about one-third of the energy used by humankind is provided from coal. The percentage of electricity generated by coal is even higher, around 45%. Almost three-fourths of the energy and coke used to make steel, the commodity commonly taken as a measure of industrial development, is provided by coal.

The general term *coal* describes a large range of solid fossil fuels derived from partial degradation of plants. Table 24.2 shows the characteristics of the major classes of coal found in the U.S., differentiated largely by percentage of fixed carbon, percentage of volatile matter, and heating value (*coal rank*). Chemically, coal is a very complex material and is by no means pure carbon. For example, a chemical formula expressing the composition of Illinois No. 6 bituminous coal is $C_{100}H_{85}S_{2.1}N_{1.5}O_{9.5}$.

Table 24.2 Major Types of Coal Found in the United States

	Proximate analysis, percent[1]				
Type of Coal	Fixed carbon	Volatile matter	Moisture	Ash	Range of heating value (Btu/pound)
Anthracite	82	5	4	9	13,000–16,000
Bituminous					
Low-volatile	66	20	2	12	11,000–15,000
Medium-volatile	64	23	3	10	11,000–15,000
High-volatile	46	44	6	4	11,000–15,000
Subbituminous	40	32	19	9	8,000–12,000
Lignite	30	28	37	5	5,500–8,000

[1] These values may vary considerably with the source of coal.

Figure 24.6 shows areas in the U.S. with major coal reserves. Anthracite, a hard, clean-burning, low-sulfur coal, is the most desirable of all coals. Approximately half of the anthracite originally present in the United States has been mined. Bituminous coal found in the Appalachian and north central coal fields has been widely used. It is an excellent fuel with a high heating value. Unfortunately, most bituminous coals have a high percentage of sulfur (an average of 2–3%), so the use of this fuel presents environmental problems. Huge reserves of virtually untouched subbituminous and

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lignite coals are found in the Rocky Mountain states and in the northern plains of the Dakotas, Montana, and Wyoming. Despite some disadvantages, the low sulfur content and ease of mining these low-polluting fuels are resulting in a rapid increase in their use, and the sight of long unit trains carrying these fuels from western states to power plants in the eastern U.S. have become very common.

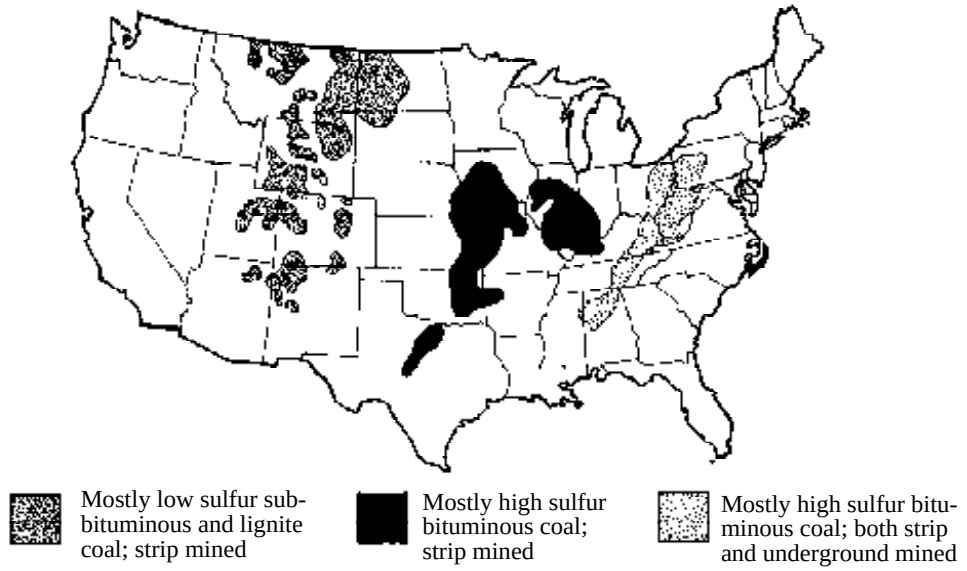


Figure 24.6 Areas with major coal reserves in the coterminous United States.

The extent to which coal can be used as a fuel depends upon solutions to several problems, including (1) minimizing the environmental impact of coal mining; (2) removing ash and sulfur from coal prior to combustion; (3) removing ash and sulfur dioxide from stack gas after combustion; (4) conversion of coal to liquid and gaseous fuels free of ash and sulfur; and, most important, (5) whether or not the impact of increased carbon dioxide emissions upon global climate can be tolerated. Progress is being made on minimizing the environmental impact of mining. As more is learned about the processes by which acid mine water is formed, measures can be taken to minimize the production of this water pollutant. Particularly on flatter lands, strip-mined areas can be reclaimed with relative success. Inevitably, some environmental damage will result from increased coal mining, but the environmental impact can be reduced by various control measures. Washing, flotation, and chemical processes can be used to remove some of the ash and sulfur prior to burning. Approximately half of the sulfur in the average coal occurs as pyrite, FeS_2, and half as organic sulfur. Although little can be done to remove the latter, much of the pyrite can be separated from most coals by physical and chemical processes.

The maintenance of air pollution emission standards requires the removal of sulfur dioxide from stack gas in coal-fired power plants. Stack gas desulfurization presents some economic and technological problems; the major processes available for it are summarized in Chapter 11, Section 11.5.

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Magnetohydrodynamic power combined with conventional steam generating units has the potential for a major breakthrough in the efficiency of coal utilization. A schematic diagram of a magnetohydrodynamic (MHD) generator is shown in Figure 24.7. This device uses a plasma of ionized gas at around 2400˚C blasting through a very strong magnetic field of at least 50,000 gauss to generate direct current. The ionization of the gas is accomplished by injecting a "seed" of cesium or potassium salts. In an MHD generator, the ultra-high-temperature gas issuing through a supersonic nozzle contains ash, sulfur dioxide, and nitrogen oxides, which severely erode and corrode the materials used. This hot gas is used to generate steam for a conventional steam power plant, thus increasing the overall efficiency of the process. The seed salts combine with sulfur dioxide and are recovered along with ash in the exhaust. Pollutant emissions are low. The overall efficiency of combined MHD-steam power plants should reach 60%, one and one-half times the maximum of present steam-only plants. Despite some severe technological difficulties, there is a chance that MHD power could become feasible on a large scale, and an experimental MHD generator was tied to a working power grid in the former Soviet Union for several years. As of the early 1990s, the U.S. Department of Energy was conducting a proof-of-concept project to help determine the practicability of magnetohydrodynamics.

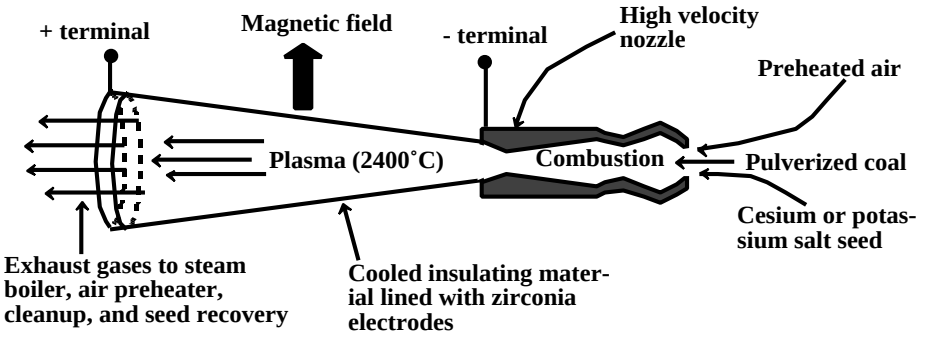


Figure 24.7 A magnetohydrodynamic power generator.

Coal Conversion

As shown in Figure 24.8, coal can be converted to gaseous, liquid, or low-sulfur, low-ash solid fuels such as coal char (coke) or solvent-refined coal (SRC). Coal conversion is an old idea; a house belonging to William Murdock at Redruth, Cornwall, England, was illuminated with coal gas in 1792. The first municipal coal-gas system was employed to light Pall Mall in London in 1807. The coal-gas industry began in the U.S. in 1816. The early coal-gas plants used coal pyrolysis (heating in the absence of air) to produce a hydrocarbon-rich product particularly useful for illumination. Later in the 1800s the water-gas process was developed, in which steam was added to hot coal to produce a mixture consisting primarily of H_2 and CO. It was necessary to add volatile hydrocarbons to this "carbureted" water-gas to bring its illuminating power up to that of gas prepared by coal pyrolysis. The U.S. had 11,000 coal gasifiers operating in the 1920s. At the peak of its use in 1947, the water-gas

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method accounted for 57% of U.S.-manufactured gas. The gas was made in low-pressure, low-capacity gasifiers that by today's standards would be inefficient and environmentally unacceptable (many sites of these old plants have been designated as hazardous-waste sites because of residues of coal tar and other wastes). During World War II, Germany developed a major synthetic petroleum industry based on coal, which reached a peak capacity of 100,000 barrels per day in 1944. A synthetic petroleum plant operating in Sasol, South Africa, reached a capacity of several tens of thousands of tons of coal per day in the 1970s.

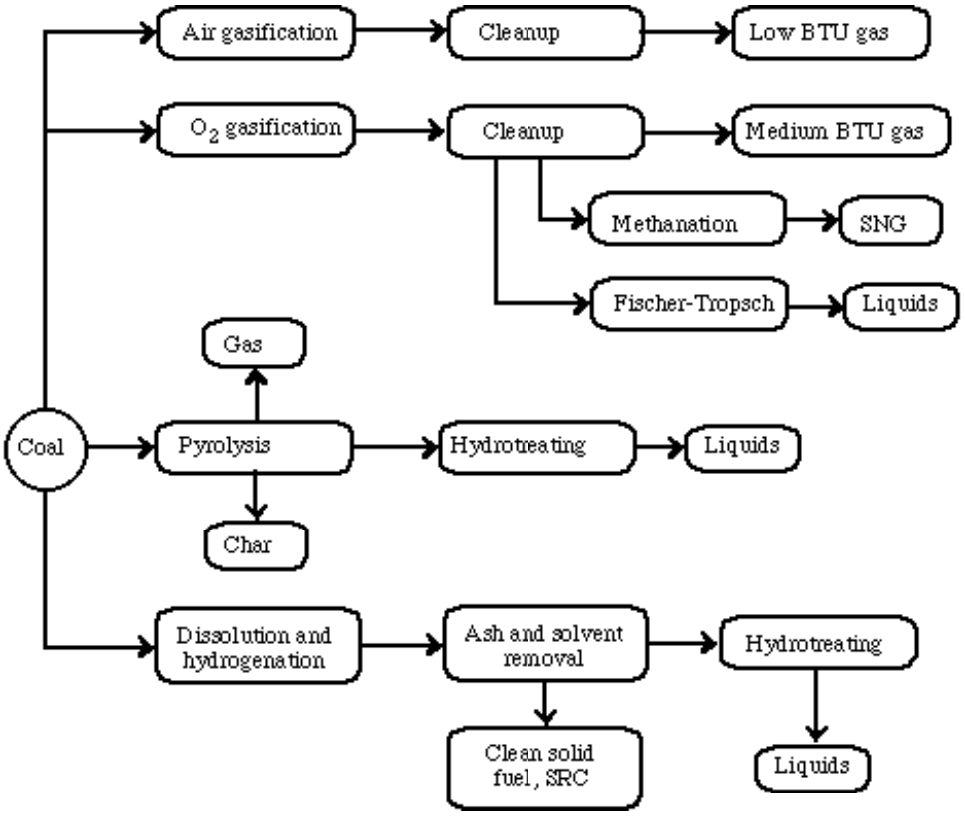


Figure 24.8 Routes to coal conversion.

The two broadest categories of coal conversion are gasification and liquefaction. Arguably the most developed route for coal gasification is the **Texaco process**, which gasifies a water slurry of coal at temperatures of 1250˚C to 1500˚C and pressures of 350 to 1200 pounds per square inch. Chemical addition of hydrogen to coal can liquefy it and produce a synthetic petroleum product. This can be done with a hydrogen donor solvent, which is recycled and itself hydrogenated with H_2 during part of the cycle. Such a process forms the basis of the successful **Exxon Donor Solvent process**, which has been used in a 250-ton/day pilot plant.

A number of environmental implications are involved in the widespread use of coal conversion. These include strip mining, water consumption in arid regions, lower overall energy conversion compared with direct coal combustion, and increased

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output of atmospheric carbon dioxide. These plus economic factors have prevented coal conversion from being practiced on a very large scale.

24.16 NUCLEAR FISSION POWER

The awesome power of the atom revealed at the end of World War II held out enormous promise for the production of abundant, cheap energy. This promise has never really come to full fruition, although nuclear energy currently provides a significant percentage of electric energy in many countries, and it may be the only source of electrical power that can meet world demand without unacceptable environmental degradation, particularly through the generation of greenhouse gases. It has been characterized as a "misunderstood" source of electricity.[2]

Nuclear power reactors currently in use depend upon the fission of uranium-235 nuclei by reactions such as

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \rightarrow {}^{133}_{51}\mathrm{Sb} + {}^{99}_{41}\mathrm{Nb} + 4\,{}^{1}_{0}\mathrm{n} \qquad (24.16.1)$$

to produce two radioactive fission products, an average of 2.5 neutrons, and an average of 200 MeV of energy per fission. The neutrons, initially released as fast-moving, highly energetic particles, are slowed to thermal energies in a moderator medium. For a reactor operating at a steady state, exactly one of the neutron products from each fission is used to induce another fission reaction in a chain reaction (Figure 24.9):

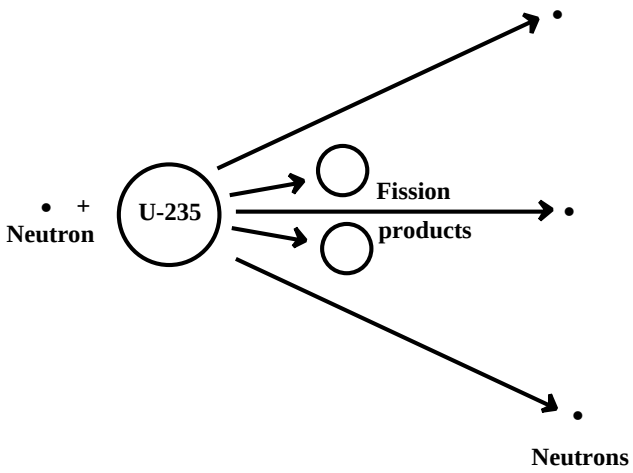


Figure 24.9 Fission of a uranium-235 nucleus.

The energy from these nuclear reactions is used to heat water in the reactor core and produce steam to drive a steam turbine, as shown in Figure 24.10.[3] As noted in Section 24.13, temperature limitations make nuclear power less efficient in converting heat to mechanical energy and, therefore, to electricity, than fossil energy conversion processes.

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A limitation of fission reactors is the fact that only 0.71% of natural uranium is fissionableuranium-235. This situation could be improved by the development of **breeder reactors**, which convert uranium-238 (natural abundance 99.28%) tofission-able plutonium-239.

A major consideration in the widespread use of nuclear fission power is the production of large quantities of highly radioactive waste products. These remain lethal for thousands of years. They must either be stored in a safe place or disposed of permanently in a safe manner. At the present time, spent fuel elements are being stored under water at the reactor sites. Eventually, the wastes from this fuel will have to be buried.

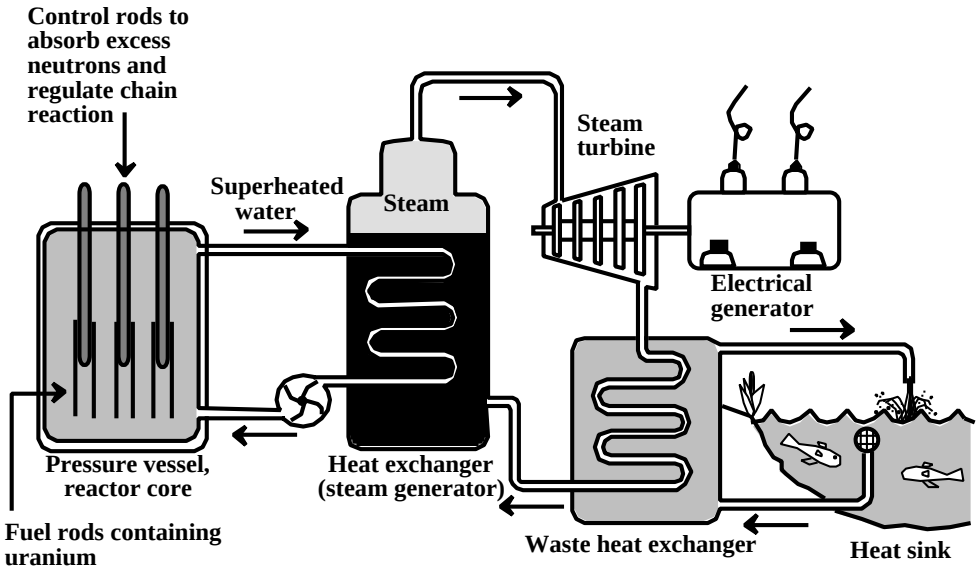


Figure 24.10 A typical nuclear fission power plant.

Another problem to be faced with nuclear fission reactors is their eventual decommissioning. There are three possible solutions. One is dismantling soon after shutdown, in which the fuel elements are removed, various components are flushed with cleaning fluids, and the reactor is cut up by remote control and buried. “Safe storage” involves letting the reactor stand 30–100 years to allow for radioactive decay, followed by dismantling. The third alternative is entombment, encasing the reactor in a concrete structure.

The course of nuclear power development was altered drastically by two accidents. The first of these occurred on March 28, 1979, with a partial loss of coolant water from the Metropolitan Edison Company’s nuclear reactor located on Three Mile Island in the Susquehanna River, 28 miles outside of Harrisburg, Pennsylvania. The result was a loss of control, overheating, and partial disintegration of the reactor core. Some radioactive xenon and krypton gases were released and some radioactive water was dumped into the Susquehanna River. In August of 1993, cleanup workers finished evaporating the water from about 8 million liters of water solution contaminated by the reactor accident, enabling the reactor building to be sealed. A much worse accident occurred at Chernobyl in the Soviet Union in April of 1986

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when a reactor blew up, spreading radioactive debris over a wide area and killing a number of people (officially 31, but probably many more).[4] Thousands of people were evacuated and the entire reactor structure had to be entombed in concrete. Food was seriously contaminated as far away as northern Scandinavia.

A much less serious, but still troublesome, nuclear accident occurred at the Tokaimura uranium processing plant in Japan on September 30, 1999, when a critical mass of enriched uranium was produced resulting in a chain reaction that exposed three workers to potentially lethal levels of radiation and contaminated 55 other workers and medical personnel. In violation of procedures, the workers used buckets to mix uranyl nitrate in a mixing tank, leading to an accumulation of about 16 kg of solution, greatly exceeding the tank's safety limit of 2.4 kg. The uranium, prepared for use in Japan's Nuclear Cycle Development Institutute's experimental fast-breeder reactor, was enriched to 18.8% fissionable ^{235}U, much higher than the 3–4% normally used in power reactors.

As of 2000, 22 years had passed since a new nuclear electric power plant had been ordered in the U.S., in large part because of the projected high costs of new nuclear plants. Although this tends to indicate hard times for the nuclear industry, pronouncements of its demise may be premature. Properly designed nuclear fission reactors can generate large quantities of electricity reliably and safely. For example, during the record summer 1993 Mississippi/Missouri River floods, many large fossil-fueled power plants were on the verge of shutting down because of disruptions of fuel supply normally delivered by river barge and train. During that time Union Electric's large Callaway nuclear plant in central Missouri ran continuously at full capacity, immune to the effects of the flood, probably saving a large area from a devastating, long-term power outage. The single most important factor that may lead to renaissance of nuclear energy is the threat to the atmosphere from greenhouse gases produced in large quantities by fossil fuels. It can be argued that nuclear energy is the only proven alternative that can provide the amounts of energy required within acceptable limits of cost, reliability, and environmental effects.

New designs for nuclear power plants should enable construction of power reactors that are much safer and environmentally acceptable than those built with older technologies. The proposed new designs incorporate built-in passive safety features that work automatically in the event of problems that could lead to incidents such as TMI or Chernobyl with older reactors. These devices—which depend upon phenomena such as gravity feeding of coolant, evaporation of water, or convection flow of fluids—give the reactor the desirable characteristics of **passive stability**. They have also enabled significant simplification of hardware, with only about half as many pumps, pipes, and heat exchangers as are contained in older power reactors.

24.17 NUCLEAR FUSION POWER

The two main reactions by which energy can be produced from the fusion of 2 light nuclei into a heavier nucleus are the deuterium-deuterium reaction,

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$$^{2}_{1}H + {}^{2}_{1}H \rightarrow {}^{3}_{2}He + {}^{1}_{0}n + 1 \text{ Mev (energy released per fusion)} \quad (24.17.1)$$

and the deuterium-tritium reaction:

$$^{2}_{1}H + {}^{3}_{1}H \rightarrow {}^{4}_{2}He + {}^{1}_{0}n + 17.6 \text{ Mev (energy released per fusion)} \quad (24.17.2)$$

The second reaction is more feasible because less energy is required to fuse the 2 nuclei than to fuse two deuterium nuclei. However, the total energy from deuterium-tritium fusion is limited by the availability of tritium, which is made from nuclear reactions of lithium-6 (natural abundance, 7.4%). The supply of deuterium, however, is essentially unlimited; one out of every 6700 atoms of hydrogen is the deuterium isotope. The ^{3}He byproduct of the fusion of 2 deuterium nuclei, Reaction 24.17.1, reacts with neutrons, which are abundant in a nuclear fusion reactor, to produce tritium required for Reaction 24.17.2.

The power of nuclear fusion has not yet been harnessed in a sustained, controlled reaction of appreciable duration that produces more power than it consumes. Most approaches have emphasized **magnetic confinement**, the "squeezing" of a plasma (ionized gas) of fusionable nuclei in a strong magnetic field. In 1994 a record power level pulse of 10.7 megawatts (MW) was achieved from the fission of deuterium with tritium by the Tokamak Fusion Test Reactor operated by Princeton University for the U.S. Department of Energy.[5] This level exceeds 20% of the power put into the reactor to achieve fusion, which of course must be boosted to well over 100% for a self-sustained fusion reactor. Within three years after this record power pulse was achieved, the Princeton Tokamak Fusion Test Reactor was shut down for lack of funding, although experiments on controlled nuclear fusion have continued at the facility and others around the world. The United States also withdrew from a huge international Tokamak project after $1 billion had been spent on the undertaking, although a consortium of European countries, Russia, and Japan continue to support the project.

An alternative to magnetic confinement is **inertial confinement**, in which a pellet composed of deuterium and tritium frozen on the inside of a plastic-coated pellet smaller than a pinhead is bombarded by laser beams or X-rays, heating the fuel pellet to a temperature of about 100 million ˚C and causing fission of the deuterium and tritium nuclei. Each such event, literally a miniature thermonuclear explosion, can release energy equivalent to the explosion of about 45 kg of TNT.

With both magnetic confinement and inertial confinement reactors, a central challenge is in harnessing the energy once it is released. Much of the energy is in the form of neutrons, which react with nuclei, such as those of iron and copper composing the reactor structure, making it radioactive and causing metal embrittlement, which would rapidly destroy the reactor. Most proposed power reactors now call for a replaceable lining, probably composed of lithium, which would absorb the neutrons and produce heat energy.

A great flurry of excitement over the possibility of a cheap, safe, simple fusion power source was generated by an announcement from the University of Utah in 1989 of the attainment of "cold fusion" in the electrolysis of deuterium oxide (heavy water). Funding was appropriated and laboratories around the world were thrown

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into frenetic activity in an effort to duplicate the reported results. Some investigators reported evidence, particularly the generation of anomalously large amounts of heat, to support the idea of cold fusion, whereas others scoffed at the idea. Since that time, cold fusion has been disproven, and the whole saga of it, described in a detailed book about the topic,[6] stands as a classic case of science gone astray.

Controlled nuclear fusion processes could be designed to produce almost no radioactive waste products. However, tritium used in the deuterium-tritium reaction is very difficult to contain, and some release of the isotope would occur. The deuterium-deuterium reaction promises an unlimited source of energy. Either of these reactions would be preferable to fission in terms of environmental considerations. Therefore, despite the possibility of insurmountable technical problems involved in harnessing fusion energy, the promise of this abundant, relatively nonpolluting energy source makes its pursuit well worth a massive effort.

24.18 GEOTHERMAL ENERGY

Underground heat in the form of steam, hot water, or hot rock used to produce steam has been used as an energy resource for about a century. This energy was first harnessed for the generation of electricity at Larderello, Italy, in 1904, and has since been developed in Japan, Russia, New Zealand, the Philippines, and at the Geysers in northern California.

Underground dry steam is relatively rare, but is the most desirable from the standpoint of power generation. More commonly, energy reaches the surface as superheated water and steam. In some cases, the water is so pure that it can be used for irrigation and livestock; in other cases, it is loaded with corrosive, scale-forming salts. Utilization of the heat from contaminated geothermal water generally requires that the water be reinjected into the hot formation after heat removal to prevent contamination of surface water.

The utilization of hot rocks for energy requires fracturing of the hot formation, followed by injection of water and withdrawal of steam. This technology is still in the experimental state, but promises approximately ten times as much energy production as steam and hot-water sources.

Land subsidence and seismic effects are environmental factors that may hinder the development of geothermal power. However, this energy source holds considerable promise, and its development continues.

24.19 THE SUN: AN IDEAL ENERGY SOURCE

Solar power is an ideal source of energy that is unlimited in supply, widely available, and inexpensive. It does not add to the earth's total heat burden or produce chemical air and water pollutants. On a global basis, utilization of only a small fraction of solar energy reaching the earth could provide for all energy needs. In the United States, for example, with conversion efficiencies ranging from 10-30%, it would only require collectors ranging in area from one tenth down to one thirtieth that of the state of Arizona to satisfy present U.S. energy needs. (This is still an enormous amount of land, and there are economic and environmental problems related to the use of even a fraction of this amount of land for solar energy collection. Certainly, many residents of Arizona would not be pleased at having so much of the state

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devoted to solar collectors, and some environmental groups would protest the resultant shading of rattlesnake habitat.)

Solar power cells (photovoltaic cells) for the direct conversion of sunlight to electricity have been developed and are widely used for energy in space vehicles. With present technology, however, they remain too expensive for large-scale generation of electricity, although the economic gap is narrowing. Most schemes for the utilization of solar power depend upon the collection of thermal energy followed by conversion to electrical energy. The simplest such approach involves focusing sunlight on a steam-generating boiler (see Illustration 6 in Figure 24.5). Parabolic reflectors can be used to focus sunlight on pipes containing heat-transporting fluids. Selective coatings on these pipes can be used so that most of the incident energy is absorbed.

The direct conversion of energy in sunlight to electricity is accomplished by special solar voltaic cells. Such devices based on crystalline silicon have operated with a 15% efficiency for experimental cells and 11–12% for commercial units, at a cost of 25–50 cents per kilowatt-hour (kWh), about 5 times the cost of conventionally generated electricity. Part of the high cost results from the fact that the silicon used in the cells must be cut as small wafers from silicon crystals for mounting on the cell surfaces. Significant advances in costs and technology are being made with thin-film photovoltaics, which use an amorphous silicon alloy. A new approach to the design and construction of amorphous silicon film photovoltaic devices uses three layers of amorphous silicon to absorb, successively, short wavelength (“blue”), intermediate wavelength (“green”), and long wavelength (“red”) light, as shown in Figure 24.11. Thin-film solar panels constructed with this approach have achievedsolar-to-electricity energy conversion efficiencies just over 10%, lower than those using crystalline silicon, but higher than other amorphousfilm devices. The low cost and relatively high conversion efficiencies of these solar panels should enable production of electricity at only about twice the cost of conventional electrical power, which would be competitive in some situations.

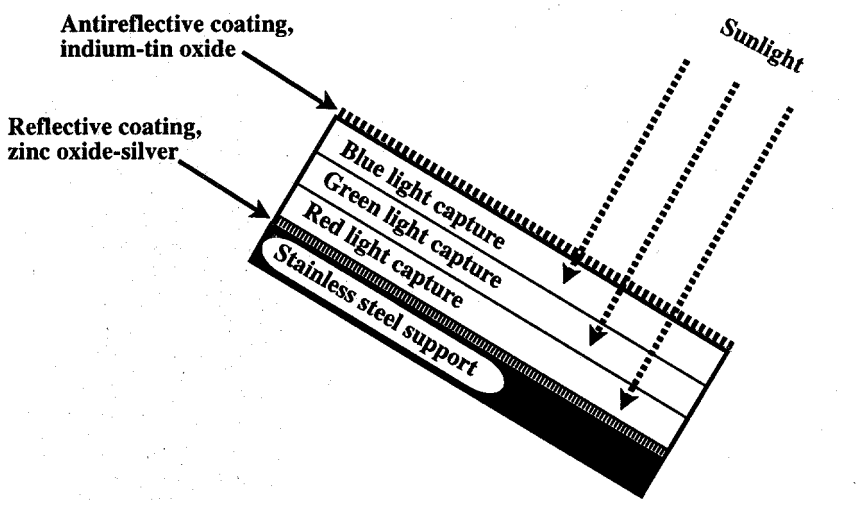


Figure 24.11 High-efficiency thin-film solar photovoltaic cell using amorphous silicon.

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A major disadvantage of solar energy is its intermittent nature. However, flexibility inherent in an electric power grid would enable it to accept up to 15% of its total power input from solar energy units without special provision for energy storage. Existing hydroelectric facilities can be used for pumped-water energy storage in conjunction with solar electricity generation. Heat or cold can be stored in water, in a latent form in water (ice) or eutectic salts, or in beds of rock. Enormous amounts of heat can be stored in water as a supercritical fluid contained at high temperatures and very high pressures deep underground. Mechanical energy can be stored with compressed air or flywheels.

Hydrogen gas, H_2, is an ideal chemical fuel that may serve as a storage medium for solar energy. Solar-generated electricity can be used to electrolyze water:

$$2H_2O + \text{electrical energy} \rightarrow 2H_2(g) + O_2(g) \qquad (24.19.1)$$

The hydrogen fuel product, and even oxygen, can be piped some distance and the hydrogen burned without pollution, or used in a fuel cell (Illustration 5 in Figure 24.5). This may make possible a "hydrogen economy." Disadvantages of hydrogen include its low heating value per unit volume and the wide range of explosive mixtures it forms with air. Although not yet economical, photochemical processes can be used to split water to H_2 and O_2 that can be used to power fuel cells.

No really insurmountable barriers exist to block the development of solar energy, such as might be the case with fusion power. In fact, the installation of solar space and water heaters became widespread in the late 1970s, and research on solar energy was well supported in the U.S. until after 1980, when it became fashionable to believe that free-market forces had solved the "energy crisis." With the installation of more heating devices and the probable development of some cheap, direct solar electrical generating capacity, it is likely that, during the coming century, solar energy will be providing an appreciable percentage of energy needs in areas receiving abundant sunlight.

The Surprising Success of Wind Power

Wind power is mentioned here because it is an indirect form of solar energy. During the 1990s, wind power emerged as a cost-competitive source of renewable energy with a remarkably high growth rate. Denmark has led other countries in establishing wind power as a significant fraction of its electrical generating capacity. Even in the United States, wind power is gaining popularity,[7] and in 1999 the U.S. set a goal of providing a significant fraction of its electricity from wind within the next two decades.

In October 1996, the largest wind farm established up to that time in Europe was opened in Carno, Wales, by National Wind Power, Ltd. This was the 32nd wind farm in Britain, which was already generating enough electricity from wind to power 150,000 homes. Producing 33.6 megawatts of power, the three-bladed turbines used to generate power at the Welsh facility are 56 meters in diameter and are mounted on towers 64 m high.

Northern regions, including parts of Alaska, Canada, the Scandinavian countries, and Russia often have consistently strong wind conditions conducive to the generation of wind power. Isolation from other sources of energy makes wind power attractive

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for many of these regions.[8] Severe climate conditions in these regions pose special challenges for wind generators. One problem can be the buildup of rime consisting of ice condensed directly on structures from supercooled fog in air.[9]

24.20 ENERGY FROM BIOMASS

All fossil fuels originally came from photosynthetic processes. Photosynthesis does hold some promise of producing combustible chemicals to be used for energy production and could certainly produce all needed organic raw materials. It suffers from the disadvantage of being a very inefficient means of solar energy collection (a collection efficiency of only several hundredths of a percent by photosynthesis is typical of most common plants). However, the overall energy conversion efficiency of several plants, such as sugarcane, is around 0.6%. Furthermore, some plants, such as *Euphorbia lathyrus* (gopher plant), a small bush growing wild in California, produce hydrocarbon emulsions directly. The fruit of the Philippine plant, *Pittsosporum reiniferum*, can be burned for illumination due to its high content of hydrocarbon terpenes (see Section 12.2), primarily α-pinene and myrcene. Conversion of agricultural plant residues to energy could be employed to provide some of the energy required for agricultural production. Indeed, until about 80 years ago, virtually all of the energy required in agriculture—hay and oats for horses, home-grown food for laborers, and wood for home heating—originated from plant materials produced on the land. (An interesting exercise is to calculate the number of horses required to provide the energy used for transportation at the present time in the Los Angeles basin. It can be shown that such a large number of horses would fill the entire basin with manure at a rate of several feet per day.)

Annual world production of biomass is estimated at 146 billion metric tons, mostly from uncontrolled plant growth. Many farm crops and trees can produce 10–20 metric tons per acre per year of dry biomass, and some algae and grasses can produce as much as 50 metric tons per acre per year. The heating value of this biomass is 5000–8000 Btu/lb for a fuel having virtually no ash or sulfur (compare heating values of various coals in Table 24.2). Current world demand for oil and gas could be met with about 6% of the global production of biomass. Meeting U.S. demands for oil and gas would require that about 6–8% of the land area of the contiguous 48 states be cultivated intensively for biomass production. Another advantage of this source of energy that is becoming increasingly important as more is learned about potential greenhouse warming is that use of biomass for fuel would not add any net carbon dioxide to the atmosphere because the carbon in the biomass fuel all comes from the atmosphere.

As it has been throughout history, biomass is significant as heating fuel, and in some parts of the world is the fuel most widely used for cooking. For example, as of the early 1990s, about 15% of Finland's energy needs were provided by wood and wood products (including black liquor by-product from pulp and paper manufacture), about 1/3 of which was from solid wood. Despite the charm of a wood fire and the sometimes pleasant odor of wood smoke, air pollution from wood-burning stoves and furnaces is a significant problem in some areas. Currently, wood provides about 8% of world energy needs. This percentage could increase through the development of "energy plantations" consisting of trees grown solely for their energy content.

Seed oils show promise as fuels, particularly for use in diesel engines, although

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these fuels may clog precision fuel injection systems in diesel engines. The most common plants producing seed oils are sunflowers and peanuts. More-exotic species include the buffalo gourd, cucurbits, and Chinese tallow tree.

Biomass could be used to replace much of the 100 million metric tons of petroleum and natural gas currently consumed in the manufacture of primary chemicals in the world each year. Among the sources of biomass that could be used for chemical production are grains and sugar crops (for ethanol manufacture), oilseeds, animal by-products, manure, and sewage (the last two for methane generation). The biggest potential source of chemicals is the lignocellulose making up the bulk of most plant material. For example, both phenol and benzene might be produced directly from lignin. Brazil has had a program for the production of chemicals from fermentation-produced ethanol.

Gasohol

A major option for converting photosynthetically produced biochemical energy to forms suitable for internal combustion engines is the production of either methanol or ethanol. Either can be used by itself as fuel in a suitably designed internal combustion engine. More commonly, these alcohols are blended in proportions of up to 20% with gasoline to give **gasohol**, a fuel that can be used in existing internal combustion engines with little or no adjustment.

Gasohol boosts octane rating and reduces emissions of carbon monoxide. From a resource viewpoint, because of its photosynthetic origin, alcohol may be considered a renewable resource rather than a depletable fossil fuel. The manufacture of alcohol can be accomplished by the fermentation of sugar obtained from the hydrolysis of cellulose in wood wastes and crop wastes. Fermentation of these waste products offers an excellent opportunity for recycling. Cellulose has significant potential for the production of renewable fuels.

Ethanol is most commonly manufactured by fermentation of carbohydrates. Brazil, a country rich in potential to produce biomass such as sugarcane, has been a leader in the manufacture of ethanol for fuel uses, with 4 billion liters produced in 1982. At one time, Brazil had over 450,000 automobiles that could run on pure alcohol, although many of these were converted back to gasoline during the era of relatively low petroleum prices since about 1980. Significant amounts of gasoline in the United States are supplemented with ethanol, more as an octane-ratings booster than as a fuel supplement.

Methanol, which can be blended with gasoline, can also be produced from biomass by the destructive distillation of wood (Section 24.9). Methanol can also be generated by converting biomass, such as wood, to CO and H_2, and synthesizing methanol from these gases.

24.21 FUTURE ENERGY SOURCES

As discussed in this chapter, a number of options are available for the supply of energy in the future. The major possibilities are summarized in Table 24.3.

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24.22 EXTENDING RESOURCES THROUGH THE PRACTICE OF INDUSTRIAL ECOLOGY

A tremendous potential exists for applying the practice of industrial ecology to lower the burden on virgin raw materials and sources of energy. As discussed in Chapter 17, Section 17.8, these approaches include using less material (dematerialization), substitution of a relatively more abundant and safe material for one that is scarce and/or toxic, extracting useful materials from wastes (waste mining), and recycling materials and items. Properly applied, these measures can not only conserve increasingly scarce raw materials, but can increase wealth as it is conventionally defined.[10] Corresponding measures can also be applied to energy resources. In recent decades, energy conservation ("de-energization"); substitution of energy sources, such as inexhaustible wind power for coal in the generation of electricity; and burning of municipal refuse to raise steam for electricity generation have reduced the need to utilize diminishing fossil energy resources and to build new power plants.

The greatest potential for extending material resources is by recycling through the practice of industrial ecology. In a sense, too, energy resources can be recycled by using otherwise waste materials to generate energy and by using heat that might otherwise go to waste for beneficial purposes, such as heating buildings.

Materials vary in their amenability to recycling. Arguably the most recyclable materials are metals in a relatively pure form. Such metals are readily melted and recast into other useful components. Among the least recyclable materials are mixed polymers or composites, the individual constituents of which cannot be readily separated. The chemistry of some polymers is such that, once they are prepared from monomers, they are not readily broken down again and reformed to a useful form. This section briefly addresses the kinds of materials that are recycled or that are candidates for recycling in a functional system of industrial ecology.

An important aspect of industrial ecology applied to recycling materials consists of the separation processes that are employed to "unmix" materials for recycling at the end of a product cycle. An example of this is the separation of graphite carbon fibers from the epoxy resins used to bind them together in carbon fiber composites. The chemical industry provides many examples where separations are required. For example, the separation of toxic heavy metals from solutions or sludges can yield a valuable metal product, leaving nontoxic water and other materials for safe disposal or reuse.

Metals

Pure metals are easily recycled, and the greatest challenge is to separate the metals into a pure state. The recycling process commonly involves reduction of metal oxides to the metal. One of the more difficult problems with metals recycling is the mixing of metals, such as occurs with metal alloys when a metal is plated onto

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Table 24.3 Possible Future Sources of Energy

Source	Principles
Coal conversion	Manufacture of gas, hydrocarbon liquids, alcohol, or solvent-refined coal (SRC) from coal
Oil shale	Retorting petroleum-like fuel from oil shale
Geothermal	Utilization of underground heat
Gas-turbine electric	Utilization of hot combustion gases in a turbine, followed by a topping cycle involving steam generation
MHD	Electricity generated by passing a hot gas plasma through a magnetic field
Thermionics	Electricity generated across a thermal gradient
Fuel cells	Conversion of chemical to electrical energy
Solar heating and cooling	Direct use of solar energy for heating and cooling through the application of solar collectors
Solar cells	Use of silicon semiconductor sheets for the direct generation of electricity from sunlight
Solar thermal electric	Conversion of solar energy to heat followed by conversion to electricity
Wind	Conversion of wind energy to electricity
Ocean thermal electric	Use of ocean thermal gradients to convert heat energy to electricity
Nuclear fission	Conversion of energy released from fission of heavy nuclei to electricity
Breeder reactors	Nuclear fission combined with conversion of nonfissionable nuclei to fissionable nuclei
Nuclear fusion	Conversion of energy released by the fusion of light nuclei to electricity
Bottoming cycles	Utilization of waste heat from power generation for various purposes
Solid waste	Combustion of trash to produce heat and electricity
Photosynthesis	Use of plants for the conversion of solar energy to other forms by a biomass intermediate
Hydrogen	Generation of H_2 by thermochemical or photochemical means for use as an energy-transporting medium

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another metal, or with components made of two or more metals in which it is hard to separate the metals. A common example of the complications from mixing metals is the contamination of iron with copper from copper wiring or other components made from copper. As an impurity, copper produces steel with inferior mechanical characteristics. Another problem is the presence of toxic cadmium used as plating on steel parts.

Recycling metals can take advantage of the technology developed over many years of technology for the separation of metals that occur together in ores. Examples of byproduct metals recovered during the refining of other metals are gallium from aluminum; arsenic from lead or copper; precious metal iridium, osmium, palladium, rhodium, and ruthenium from platinum; and cadmium, germanium, indium, and thorium from zinc.

Plastics

Much attention has been given to the recycling of plastics in recent years. Compared with metals, plastics are much less recyclable because recycling is technically difficult and plastics are less valuable than metals. There are two general classes of plastics, a fact that has a strong influence upon their recyclability. Thermoplastics are those that become fluid when heated and solid when cooled. Since they can be heated and reformed multiple times, thermoplastics are generally amenable to recycling. Recyclable thermoplastics include polyalkenes (low-density and high-density polyethylene and polypropylene); polyvinylchloride (PVC), used in large quantities to produce pipe, house siding, and other durable materials; polyethylene terephthalate; and polystyrene. Plastic packaging materials are commonly made from thermoplastics and are potentially recyclable. Fortunately, from the viewpoint of recycling, thermoplastics make up most of the quantities of plastics used.

Thermosetting plastics are those that form molecular cross linkages between their polymeric units when they are heated. These bonds set the shape of the plastic, which does not melt when it is heated. Therefore, thermosetting plastics cannot be simply remolded; they are not very amenable to recycling, and often burning them for their heat content is about the only use to which they can be put. An important class of thermosetting plastics consists of the epoxy resins, characterized by an oxygen atom bonded between adjacent carbons (1,2-epoxide or oxirane). Epoxies are widely used in composite materials combined with fibers of glass or graphite. Other thermosetting plastics include cross-linked phenolic polymers, some kinds of polyesters, and silicones. When recycling is contemplated, the best use for thermosetting plastics is for the fabrication of entire components that can be recycled.

Contaminants are an important consideration in recycling plastics. A typical kind of contaminant is paint used to color the plastic object. Adhesives and coatings of various kinds may also act as contaminants. Such materials can weaken the recycled material or decompose to produce gases when the plastic is heated for recycling. Toxic cadmium used to enable polymerization of plastics, a “tramp element” in recycling parlance, can hinder recycling of plastics and restrict the use of the recycled products.

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Lubricating Oil

Lubricating oils are used in vast quantities and are prime candidates for recycling. The simplest means of recycling lubricating oil is to burn it, and large volumes of oil are burned for fuel. This is a very low level of recycling and will not be addressed further here.

For many years, the main process for reclaiming waste lubricating oil used treatment with sulfuric acid followed by clay. This process generated large quantities of acid sludge and spent clay contaminated with oil. These undesirable byproducts contributed substantial amounts of wastes to hazardous-waste disposal sites. Current state-of-the-art practicesof lubricating oil reclamation do not utilize large quantities of clay for cleanup, but instead use solvents, vacuum distillation, and catalytic hydrofinishing to produce a usable material from spent lubricating oil.[11] The first step is dehydration to remove water and stripping to remove contaminant fuel (gasoline) fractions. If solvent treatment is used, the oil is then extracted with a solvent, such as isopropyl or butyl alcohols or methylethyl ketone. After treatment with a solvent, the waste oil is commonly centrifuged to remove impurities that are not soluble in the solvent. The solvent is then stripped from the oil. The next step is a vacuum distillation that removes a light fraction useful for fuel and a heavy residue. The lubricating oil can then be subjected to hydrofinishing over a catalyst to produce a suitable lubricating oil product.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

The two major kinds of sources of materials are those from [1]_____ _____ sources. [2]_____ is a term used to refer to quantities of materials or energy that are estimated to be *ultimately* available, whereas [3]_____ is a term that refers to well-identified resources that can be profitably utilized with existing technology. Some kinds of mineral deposits include [4] . An enriched deposit of a metal is called [5]_____, the value of which is expressed in terms of a [6]_____ defined mathematically as [7]_____.
One of the more environmentally troublesome by-products of mineral refining consists of [8]_____. Aluminum is obtained from a mineral called [9] in which aluminum is contained in the compound [10]_____.
The metal [11]_____ is of crucial importance because of its use in stainless steel and superalloys. Two environmental problems with the extraction of copper are [12]_____ _____. About 2/3 of the lead in batteries is [13]_____. A use of zinc that has extended the life of automobile bodies and frames is as a [14]_____ _____. Potassium is of special importance because of its use as [15]_____. A common secondary

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mineral that is used for applications such as in making refractories is [16]_____. The cheapest mineral commodities per ton, although of high value because of the enormous quantities used are [17]_____. The most common phosphate minerals are [18]_____ _____. An important nonmetal now largely recovered as byproduct, such as from natural gas, is [19]_____. The chemical formula of a mineral used to make plasterboard is [20]_____. A valuable renewable resource largely composed of solid polysaccharides is [21]_____. At present, most of the energy consumed by humans is produced from [22]_____ _____ of which the greatest fraction is in the form of [23]_____. [24]_____ is the economic sector with the greatest potential for increased energy efficiency. The efficiency of the conversion thermal energy to mechanical energy in a heat engine is expressed by [25]_____. A recovery efficiency of 60% through secondary or tertiary techniques could [26]_____ _____ the amount of available petroleum. The percentage of electricity generated by coal is around [27]_____. Different kinds of coal are commonly classified according to [28]_____. Starting with the production of coal gas, conversion of coal to more desirable fuels has been practiced for about [29]_____ years. Nuclear fission energy is commonly released by [30]_____ _____ when they absorb neutrons. Available energy from uranium could be greatly increased by the use of [31]_____. Modern nuclear reactors that depend upon phenomena such as gravity feeding of coolant, evaporation of water, or convection flow of fluids give the reactor the desirable characteristics of [32]_____. The reaction

$$ {}_{1}^{2}\mathrm{H} + {}_{1}^{3}\mathrm{H} \rightarrow {}_{2}^{4}\mathrm{He} + {}_{0}^{1}\mathrm{n} + 17.6\ \mathrm{Mev} $$

shows generation of [33]_____ energy. Larderello, Italy, and the Geysers in northern California both have sources of [34]_____ energy. The direct conversion of energy in sunlight to electricity is accomplished by devices called [35]_____. Disadvantages of using hydrogen as a fuel are [36] _____. A pollution-free source of renewable energy now widely utilized in Denmark is [37]___ _____. Ideally, current world demand for oil and gas could be met with about [38]_____ of the global production of biomass. Currently, wood provides about [39]_____ of world energy needs. Compared with conventional gasoline, gasohol boosts [40]_____ and reduces emissions of [41]_____ _____. One of the more difficult problems with metals recycling is the [42]_____. Plastics are much less recyclable than metal because [43] _____. Current state-of-the-art practicesof lubricating oil reclamation use [44]_____ _____ to produce a usable material from spent lubricating oil. Formerly, the main process for reclaiming waste lubricating oil used [45]_____, a process that [46]_____.

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Answers to Chapter Summary

1. extractive and renewable
2. resources
3. reserves
4. hydrothermal deposits, sedimentary deposits, evaporites, placer deposits
5. an ore
6. concentration factor
7. (concentration of material in ore)/(average crustal concentration)
8. waste tailings
9. bauxite
10. Al_2O_3
11. chromium
12. its dilute form and its occurrence as the sulfide
13. recycled
14. corrosion-resistant coating on steel
15. fertilizer
16. clay
17. sand and gravel
18. hydroxyapatite, $Ca_5(PO_4)_3(OH)$, and fluorapatite, $Ca_5(PO_4)_3F$
19. sulfur
20. $CaSO_4 \cdot 2H_2O$
21. wood
22. fossil fuels
23. coal or lignite
24. Transportation
25. the Carnot equation
26. double
27. 45%
28. rank
29. 200
30. the splitting of uranium nuclei
31. breeder reactors
32. passive stability
33. nuclear fusion
34. geothermal
35. solar voltaic cells
36. its low heating value per unit volume and the wide range of explosive mixtures it forms with air
37. wind energy
38. 6%
39. 8%
40. octane rating
41. carbon monoxide
42. mixing of metals
43. recycling is technically difficult and plastics are less valuable
44. solvents, vacuum distillation, and catalytic hydrofinishing
45. treatment with sulfuric acid followed by clay
46. generated large quantities of acid sludge and spent clay contaminated with oil

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QUESTIONS AND PROBLEMS

1. What pollution control measures may produce a shortage of platinum metals?
2. List and discuss some of the major environmental concerns related to the mining and utilization of metal ores.
3. What are the major phosphate minerals?
4. Arrange the following energy conversion processes in order from the least to the most efficient: (a) electric hot water heater, (b) photosynthesis, (c) solar cell, (d) electric generator, (e) aircraft jet engine.
5. Considering the Carnot equation and common means for energy conversion, what might be the role of improved materials (metal alloys, ceramics) in increasing energy conversion efficiency?
6. Why is shale oil, a possible substitute for petroleum in some parts of the world, considered to be a pyrolysis product?
7. List some coal ranks and describe what is meant by coal rank.
8. In the 1800s and early 1900s, why were hydrocarbons added to gas produced by reacting steam with hot carbon from coal to make a useful gas product?
9. What is the principle of the Exxon Donor Solvent process for producing liquid hydrocarbons from coal?
10. As it is now used, what is the principle or basis for the production of energy from uranium by nuclear fission? Is this process actually used for energy production? What are some of its environmental disadvantages? What is one major advantage?
11. What would be at least two highly desirable features of nuclear fusion power if it could ever be achieved in a controllable fashion on a large scale?
12. Justify describing the sun as “an ideal energy source.” What are two big disadvantages of solar energy?
13. What are some of the greater implications of the use of biomass for energy? How might such widespread use affect greenhouse warming? How might it affect

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agricultural production of food?

14. Describe how gasohol is related to energy from biomass.
15. How does the trend toward utilization of less-rich ores affect the environment? What does it have to do with energy utilization?
16. Of the resources listed in this chapter, list and discuss those that are largely from by-product sources.
17. Why is the total dollar value of “cheap” sand and gravel so high? What does this fact imply for environmental protection?

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Manahan, Stanley E. "FUNDAMENTALS OF ANALYTICAL CHEMISTRY"
Fundamentals of Environmental Chemistry
Boca Raton: CRC Press LLC, 2001

25 FUNDAMENTALS OF ANALYTICAL CHEMISTRY

25.1 NATURE AND IMPORTANCE OF CHEMICAL ANALYSIS

Analytical chemistry is that branch of the chemical sciences employed to determine the composition of a sample of material. A **qualitative analysis** is performed to determine *what* is in a sample. The amount, concentration, composition, or percent of a substance present is determined by **quantitative analysis**. Sometimes both qualitative and quantitative analyses are performed as part of the same process.

Analytical chemistry is important in practically all areas of human endeavor and in all spheres of the environment. Industrial raw materials and products processed in the anthrosphere are assayed by chemical analysis, and analytical monitoring is employed to monitor and control industrial processes. Hardness, alkalinity, and trace-level pollutants (see Chapters 11 and 12) are measured in water by chemical analyses. Nitrogen oxides, sulfur oxides, oxidants, and organic pollutants (see Chapters 15 and 16) are determined in air by chemical analysis. In the geosphere (see Chapters 17 and 18), fertilizer constituents in soil and commercially valuable minerals in ores are measured by chemical analysis. In the biosphere, xenobiotic materials and their metabolites (see Chapter 23) are monitored by chemical analysis.

Analytical chemistry is a dynamic discipline. New chemicals and increasingly sophisticated instruments and computational capabilities are constantly coming into use to improve the ways in which chemical analyses are done. Some of these improvements involve the determination of ever smaller quantities of substances; others greatly shorten the time required for analysis; and some enable analysts to tell with much grater specificity the identities of a large number of compounds in a complex sample.

Understanding some of the material in Chapter 1 is essential to understanding and practicing analytical chemistry. A good understanding of numbers, their meanings, their uncertainties, and calculations involving numbers are essential for the practice of analytical chemistry. These concepts are discussed in Sections 1.6 and

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1.7. Analytical chemistry is a science of measurement. Therefore, basic concepts of chemical measurement discussed in Sections 1.8–1.13 must be mastered before studying analytical chemistry. Calculating and expressing the results of a chemical analysis must be done accurately and with a thorough knowledge of units, unit conversion factors, and their use in computations, as discussed in Section 1.14. Chemical analysis requires the proper use of laboratory apparatus. Crucial laboratory apparatus used in analytical chemistry include the laboratory balance for accurate mass measurement and volumetric glassware, specifically the pipet, buret, and volumetric flask shown in Figure 1.10.

Many of the calculations of analytical chemistry involve quantities of materials that take part in chemical reactions. Therefore, stoichiometric calculations may be very important in analytical chemistry. The reader should refer back to stoichiometry in Chapter 5.

This chapter is written to provide an overview of analytical chemistry. Chapter 26, "Environmental and Xenobiotics Analysis," covers some specific aspects of the analysis of environmental samples of various kinds. For those users who may become directly involved in doing chemical analyses, more-detailed coverage of the topic and specific analytical procedures are discussed in reference works listed at the end of the chapter.

25.2 THE CHEMICAL ANALYSIS PROCESS

It is important to regard chemical analysis within the framework of an overall *chemical analysis process*, rather than an isolated "laboratory experiment." Each step in the analysis process is crucial to getting accurate and meaningful results. Figure 25.1 outlines the process.

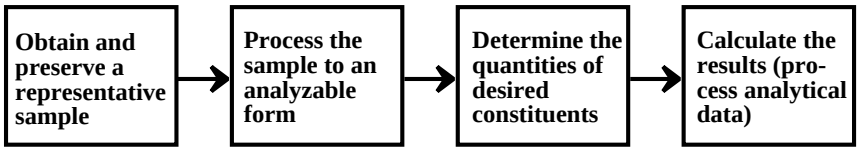


Figure 25.1 Schematic representation of the major steps involved in the chemical analysis process.

The first step in the analytical process is to obtain a representative **sample** or samples, that portion of matter upon which the analysis is performed. The sample should be a **representative sample**, the composition of which is as close as possible to the whole mass of whatever is being analyzed. Obtaining a good sample is a crucial step in the chemical analysis process. Failure to obtain and properly preserve a good sample means that the whole analysis may be incorrect, rendering all the other steps involved worthless.

Sample processing is performed to get the sample into a form that can be analyzed. For a few kinds of analysis, the sample is analyzed without further processing or after minimal steps, such as grinding and mixing. Often, sample processing requires putting the sample into solution. Sample dissolution can be as simple as stirring a soil sample with hydrochloric acid to dissolve potassium required

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for soil fertility. Or it can be complicated and severe, such as oxidizing and dissolving fish tissue for metals analysis with a hot concentrated mixture of HNO_3 and $HClO_4$.

The discussion of sample processing above leads to the definition of two kinds of analyses, depending upon what is done with the sample. When a sample is oxidized, dissolved in acid, or otherwise greatly altered as part of the analytical process, the chemical analysis is termed *destructive.* In some cases, such as those where evidence of a crime is involved, it is important to preserve the sample in an unaltered form. This requires *nondestructive* methods of analysis, such as can be performed by making the sample radioactive by irradiation with neutrons in a nuclear reactor and measuring the energies and intensities of gamma radiation given off by the activated elements (neutron activation analysis).

After sample processing, it is often necessary to eliminate **interferences** from substances in the sample that can cause erroneous results. This can be done by removing interfering substances or by treating the sample with substances that react with interferences to render them non-interfering.

After all the steps outlined above have been performed, the actual measurement of whatever is being determined is performed. The substance that is measured, such as calcium in a water sample or *trans*,*trans*-muconic acid measured in blood as evidence of occupational exposure to toxic benzene, is called the **analyte**. The specific measurement of the analyte is referred to as a **determination**, whereas the total process to which the sample is subjected is called an **analysis**.

The final step in a chemical analysis is **calculation** of results. This step may consist of a few simple calculations, or it may involve a complicated data processing operation that calculates analyte levels and compensates for interferences in the method. In addition to providing a number for the quantity or percentage of analyte in a sample, the calculation of results usually involves an evaluation of the reliability of the data (precision and accuracy) of the analytical values. In modern analytical laboratories, results are calculated and stored by computer, frequently as part of the process by which analyte levels are measured with an appropriate instrument.

25.3 MAJOR CATEGORIES OF CHEMICAL ANALYSIS

Both qualitative and quantitative analysis are divided between **classical** methods involving primarily chemical reactions and simple measurements of mass and volume, and **instrumental methods** that use instruments of varying degress of complexity and sophistication to measure quantities of analyte. Classical methods are often **wet chemical** procedures using reagents in solution and reactions of dissolved analyte. Instrumental methods use various devices to measure physical manifestations of chemical species and chemical reactions, such as absorption of light, electrical potentials, or small changes in temperature.

Analytical chemistry can also be divided between **chemical** and **physical** methods of analysis. Chemical methods almost always involve the measurement of a mass of a chemical species or volume of a reagent solution produced or consumed by a chemical reaction. For example, the acid in an acid mine water sample can be determined by adding exactly enough of a solution of base of accurately known concentration to exactly neutralize the strong acid in the sample,

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$$H^+ + Na^+ + OH^- \rightarrow H_2O + Na^+ \quad (25.3.1)$$

exactly measuring the amount of NaOH required, and calculating the quantity of acid neutralized; such a procedure is an acid-base **titrimetric** procedure.

Physical methods of analysis normally involve a measurement of a physical parameter other than mass or volume. For example, a water sample suspected of being polluted with hexavalent chromium can be injected into an inductively coupled plasma atomic emission spectrometer and the intensity of light given off by very hot chromium atoms emitted by the sample measured to give the chromium concentration. Or fluoride in a water sample can be determined by measuring the potential versus a reference electrode of a fluoride ion-selective electrode immersed in the sample and comparing that value with the potential measured in a standard F^- solution to give the value of $[F^-]$.

25.4 ERROR AND TREATMENT OF DATA

A chemical analysis is only as good as the numbers that go into calculating and expressing the result. Therefore, data analysis is a crucial aspect of chemical analysis. All analytical measurements are subject to greater or lesser degrees of error. So every reasonable effort is made to reduce the amount of error in an analytical measurement. Since some error is inevitable, it is important to know the degree of error and express it correctly in the final result.

One of the major objectives of analytical measurements is to obtain *reproducible results*. For example, if three determinations of the percentage of iron in the same iron ore sample gave values of 18.76, 18.71, and 18.73 percent, the analyst would have a relatively high degree of confidence in the validity of the results because the three values are so close together. The degree to which numbers in a group of analytical results are in agreement with each other is the **precision** of the group of numbers. A lack of precision may indicate the presence of **indeterminate**, or **random**, **errors**. Such errors vary randomly in direction and magnitude and are from sources that cannot be determined.

However, just because the results of a set of analyses are in close agreement does not necessarily mean that the values are correct. This is because of the possibility of **determinate errors**. Such errors have a definite cause (although it may be unknown to the analyst), and each type of determinate error is always in the same direction. For example, if an analytical chemist were using a pipet rated to deliver 25.00 mL of solution that through a manufacturing mistake actually delivered 25.35 mL, a determinate error would be introduced into the analysis; in this case, it could readily be detected by calibrating the pipet.

The extent to which the data or the average value of a set of data agree with the true value being determined is the **accuracy** of the data. The relationship between accuracy and precision is shown graphically in Figure 25.2. Although the average of a set of randomly scattered, imprecise results may be close to the true value, normally the average of a set of imprecise results is inaccurate as well.

In doing analytical calculations and expressing analytical results, it is important to know and correctly handle and express the **uncertainties** of the numbers used, a

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concept discussed in Chapter 1, Section 1.7. For example, a skilled analyst can read the volume delivered by a laboratory buret to the nearest 0.01 mL. Therefore, a volume expressed as 36.27 mL implies that the volume is within ± 0.01 mL of 36.27 mL and has an uncertainty of 0.01 mL. It would be incorrect to express the volume 36.270 mL because it is not known to the nearest 0.001 mL as that number would imply. It would also be incorrect to express the volume as 36.3 mL because the value is known more accurately than ± 0.1 mL. In calculations involving measured laboratory quantities the rules for handling significant figures as discussed in Section 1.7 must be followed.

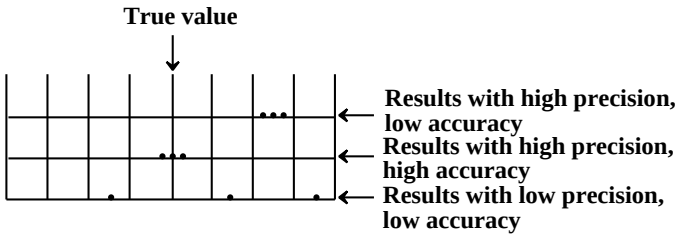


Figure 25.2 Representation of precision and accuracy. Each solid circle, •, stands for an experimentally determined value.

The uncertainty of a number from an analytical measurement, such as the ± 0.01 mL discussed above, is the **absolute uncertainty** of the measurement. The **relative uncertainty** of a measured value is given by the equation

$$\text{Relative uncertainty} = \frac{\text{Absolute uncertainty}}{\text{Measured value}} \qquad (25.4.1)$$

Commonly, relative uncertainty is expressed in parts per thousand (ppt) a value given by multiplying the result of the above equation by 1000. In the example of the volume of 36.27 mL delivered by a buret as discussed above, the relative uncertainty in parts per thousand is

$$\text{Relative uncertainty} = \frac{0.01\ \text{mL}}{36.27\ \text{mL}} \times 1000 = 0.3\ \text{ppt} \qquad (25.4.1)$$

If the buret had been used to deliver only 1.52 mL, the absolute uncertainty would still be 0.01 mL, but the relative uncertainty would be the following:

$$\text{Relative uncertainty} = \frac{0.01\ \text{mL}}{1.52\ \text{mL}} \times 1000 = 6\ \text{ppt} \qquad (25.4.1)$$

The relative uncertainty in measuring the smaller volume is much greater. That is why in such measurements it is generally more accurate to measure a larger quantity, when it is possible to do so.

Error and the uncertainty that it adds to analytical calculations are very important aspects of analytical chemistry. It is beyond the scope of this book to discuss those concepts in detail. However, any reader required to do chemical analysis and the calculations resulting therefrom should consult more-extensive works dealing with the topic.

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25.5 GRAVIMETRIC ANALYSIS

Conceptually the most straightforward kind of quantitative analysis, **gravimetric analysis** consists of isolating in a pure form a species produced stoichiometrically by the analyte, weighing it, and calculating the percentage of analyte in the sample. Obtaining a pure, weighable product is often a complicated process. A number of ways of doing that have been developed. The most common of these is formation of a precipitate by a reaction of the analyte in solution. As an example, the chloride content of a weighed, water-soluble sample can be determined by precipitating the chloride in the dissolved sample with excess silver nitrate solution:

$$\underbrace{Ag^+(aq) + NO_3^-(aq)}_{\text{Silver nitrate reagent}} + \underbrace{Cl^-(aq)}_{\text{Chloride analyte}} \rightarrow \underbrace{AgCl(s)}_{\text{Silver chloride precipitate}} + NO_3^-(aq) \qquad (25.5.1)$$

The silver chloride precipitate, which can be produced in a very pure form, is collected on a weighed filter crucible (Figure 25.3) and washed to remove extraneous residual salts. After drying to remove excess water, the crucible and precipitate are weighed to get the mass of precipitate and the percentage of chloride is calculated by stoichiometric calculation. Where the atomic mass of chloride is 35.45 g/mol and the molar mass of AgCl is 143.32 g/mol, the calculation is

$$\text{Mass chloride} = \text{mass AgCl} \times \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} \times \frac{1 \text{ mol } Cl^-}{1 \text{ mol AgCl}} \times \frac{35.45 \text{ g } Cl^-}{1 \text{ mol Cl}} \qquad (25.5.2)$$

$$\text{Percent chloride} = \frac{\text{mass chloride}}{\text{mass sample}} \times 100 \qquad (25.5.3)$$

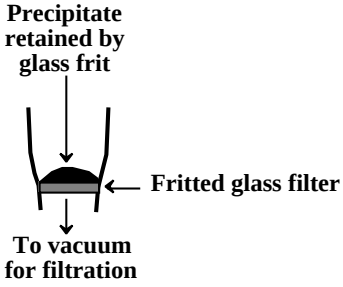


Figure 25.3 Filter crucible used to collect and weigh precipitates for gravimetric analysis.

Suppose, for example, that a 1.2643 g sample containing chloride yielded 0.9285 g of AgCl precipitate. The percentage of chloride in the sample is

$$\text{Mass chloride} = 0.9285 \text{ g AgCl} \times \frac{1 \text{ mol AgCl}}{143.32 \text{ g AgCl}} \times \frac{1 \text{ mol } Cl^-}{1 \text{ mol AgCl}} \times \frac{35.45 \text{ g } Cl^-}{1 \text{ mol Cl}}$$

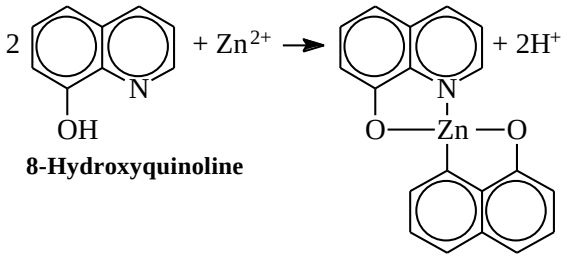
$$\text{Mass chloride} = 0.2297 \text{ g}$$

$$\text{Percent chloride} = \frac{0.2997 \text{ g}}{1.2643 \text{ g}} \times 100 = 18.17\%$$

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Over the decades before more-modern instrumental methods of analysis were developed, gravimetric techniques were developed for a wide range of analytes. Examples include sulfate determined by precipitating $BaSO_4$ with $BaCl_2$ reagent; calcium precipitated as the oxalate CaC_2O_4, which, in turn, could be heated to produce weighable $CaCO_3$ or CaO; and magnesium precipitated as an ammonium phosphate salt, then heated to produce $Mg_2P_2O_7$.

The versatile nature of organic chemistry led to a number of organic reagents used to form precipitates with analytes, especially metals. One widely used reagent was 8-hydroxyquinoline shown forming a precipitate with zinc ion in the reaction below:



8-Hydroxyquinoline

Precipitate of the 8-hydroxyquinolate chelate of zinc(II)

(25.5.4)

Two 8-hydroxyquinoline anions (formed by loss of H^+) bind with Zn^{2+} ion as shown above to produce a chelate species (see Chapter 11, Section 11.9) that can be weighed to calculate the amount of zinc in the sample. Organic precipitants with high molar masses, such as 8-hydroxyquinoline, offer an advantage for gravimetric analysis in that they produce a relatively high mass of precipitate from comparatively little analyte. Higher masses of precipitates translate to less relative error in weighing, thus increasing the accuracy of the determination.

One of the simplest gravimetric techniques in those limited cases where it is applicable is the precipitation of a metal from solution by electrodeposition onto a cathode. A good example is the determination of copper, which can be plated onto a weighed platinum electrode by the following electrochemical half-reaction:

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s) \qquad (25.5.5)$$

weighing the platinum electrode after electrodeposition is complete gives a mass of copper that can then be used to calculate the percentage of copper in the sample.

In some cases, gravimetric analysis can be performed by collecting a gas given off by a chemical reaction and weighing it. One of the classic methods for determining the percentage of carbon in an organic species is to oxidize the organic to convert the carbon to CO_2, collect the carbon dioxide given off quantitatively, and weigh it in the collection tube. Volatile matter contents of samples can be determined by weighing a sample before and after heating, with the difference being the mass of volatile matter in the sample. One such means of gravimetric analysis still widely applied is the gravimetric determination of water in a solid sample by this

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method.

Although gravimetric analysis is now largely of historical interest, it remains a versatile analytical technique. In addition to being applicable to a wide range of analytes, gravimetric analysis is capable of giving highly accurate results.

25.6 VOLUMETRIC ANALYSIS: TITRATION

Other than gravimetric analysis, the other major type of classical "wet chemical" analysis technique consists of measuring the volume of a reagent required to react with an analyte. Such a procedure is called **titration**, which involves the following:

- A measured quantity of sample that may consist of a weighed quantity of a solid, or a measured volume of a solution and the unknown, is placed in solution.
- A **standard solution** of known concentration of a reagent that reacts quantitatively with the analyte is added to the unknown with a buret so that the volume of standard solution can be measured accurately.
- An **indicator** consisting of a dye that changes color, or some other means, is used to detect an **end point**, the experimental representation of the **equivalence point** at which exactly the stoichiometric amount of reagent required to react with analyte occurs. The volume at which the end point occurs is recorded from the buret.
- The quantity or concentration of analyte is calculated from the stoichiometry of the titration reaction.

The most common type of titration reaction consists of acid-base titration in which an unknown quantity or concentration of acid is titrated with standard base or vice versa. For example, a solution of hydrochloric acid of unknown concentration can be titrated with a standard solution of sodium hydroxide base using as an indicator phenolphthalein, which changes from colorless to pink at the end point. The physical steps involved in the titration are shown in Figure 25.4. The reaction between the HCl and NaOH is the following:

$$\underset{\text{Hydrochloric acid analyte}}{H^+ + Cl^-} + \underset{\text{sodium hydroxide titrant}}{Na^+ + OH^-} \rightarrow H_2O + Na^+ + Cl^- \qquad (25.6.1)$$

Before the end point, there is excess H^+, so the pH is less than 7 (see Section 6.6 for a discussion of pH and the pH values in acidic and basic solutions). Beyond the end point, there is excess base, and the pH is greater than 7. Since HCl is a strong (completely ionized) acid and NaOH is a strong (completely ionized) base, the pH at the end point is exactly 7. (See Section 6.4 for a discussion of strong and weak acids and bases.) Furthermore, the pH changes very markedly by several pH units with the addition of just a few drops of sodium hydroxide titrant at a volume that is in the immediate vicinity of the end point. This change is reflected by the abrupt change in color of the phenolphthalein indicator from colorless to pink at the end point, where the addition of titrant is stopped, and the end point volume recorded.

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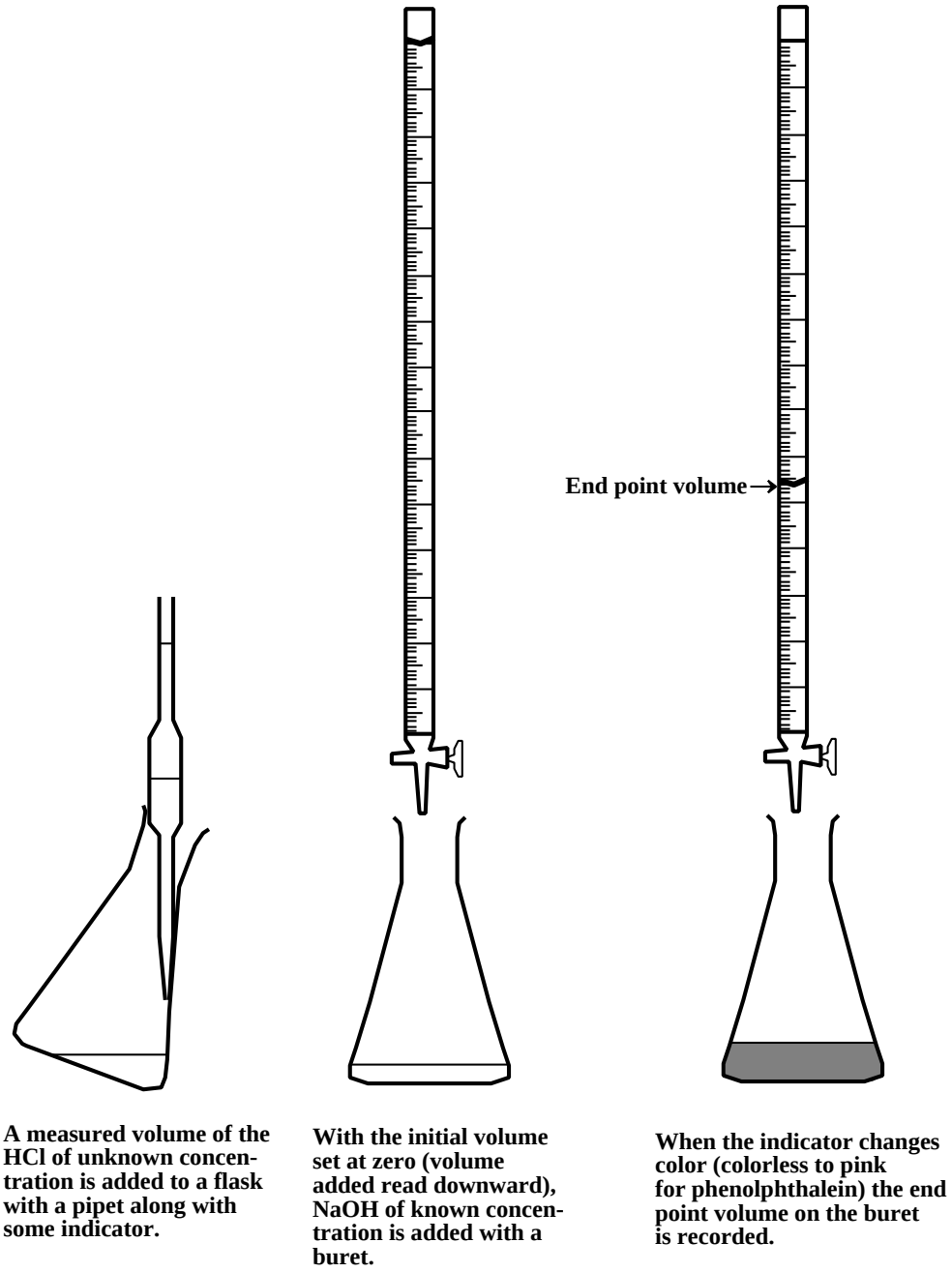


Figure 25.4 Steps in the titration of an unknown HCl solution with standard NaOH.

As noted in the preceding discussion, the course of acid-base titrations is reflected by the pH of the solution in the reaction flask as titrant is added. By using a device called a pH meter, the pH can be recorded and plotted as a function of added titrant. The result is a **titration curve** (Figure 25.5).

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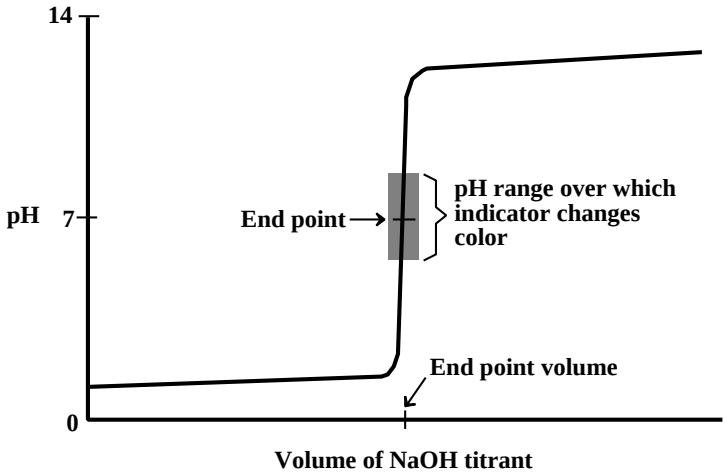


Figure 25.5 Titration curve as a plot of pH versus volume of titrant for the titration of HCl with NaOH titrant. A indicator changes color over a pH range, which indicates the end point.

Stoichiometry is the basis of calculations in titrimetric analysis. In the reaction,

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow H_2O + Na^+ + Cl^- \qquad (25.6.1)$$

there is a 1/1 mole ratio of NaOH added to HCl in the sample at the end point, so the following relationship holds:

$$\text{Moles HCl} = \text{moles NaOH} \qquad (25.6.2)$$

From the definition of molarity, where M is the molar concentration and volume is in liters, the equations

$$M_{HCl} = \frac{\text{moles HCl}}{\text{Volume HCl}}, \text{ Moles HCl} = M_{HCl} \times (\text{Volume HCl}) \qquad (25.6.3)$$

and

$$M_{NaOH} = \frac{\text{moles NaOH}}{\text{Volume NaOH}}, \text{ Moles NaOH} = M_{NaOH} \times (\text{Volume NaOH}) \qquad (25.6.4)$$

relate the molar concentrations and volumes of HCl and NaOH. From the equations above, the concentration of a sample of HCl of carefully measured volume titrated with NaOH of known concentration and measured with a buret is given by the following:

$$M_{HCl} = \frac{(\text{Volume NaOH}) \times M_{NaOH}}{\text{Volume HCl}} \qquad (25.6.5)$$

Example: A 50.0 mL sample of HCl required 42.53 mL of 0.1005 M NaOH for titration. What was the concentration of HCl?

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$$M_{HCl} = \frac{(\text{Volume NaOH}) \times M_{NaOH}}{\text{Volume HCl}} = \frac{0.04253\ \text{L} \times 0.1005\ \text{mol/L}}{0.05000\ \text{L}}$$

$$= 0.0855\ \text{mol/L}$$

Titration can also be used to determine percentage composition of samples. For example, consider that a 1.136 g sample containing solid NaOH and inert material was weighed out, dissolved and titrated with 0.1036 M standard HCl, of which 48.61 mL was required. What was the percentage of NaOH, molar mass 40.0, in the sample? At the end point, the number of moles of NaOH in the sample exactly equals the number of moles of HCl added. But, because the NaOH is in a solid and the mass of NaOH is needed to calculate the percentage of it in the sample, the following equation can be used:

$$\frac{\text{Mass NaOH}}{\text{molar mass NaOH}} = \text{mol NaOH} = \text{mol HCl} = (\text{Volume HCl}) \times M_{HCl} \qquad (25.6.6)$$

$$\text{Mass NaOH} = (\text{molar mass NaOH}) \times (\text{Volume HCl}) \times M_{HCl}$$

$$\text{Mass NaOH} = 40.0\ \text{g/mol} \times 0.04861\ \text{L} \times 0.1306\ \text{mol/L}$$

$$= 0.254\ \text{g NaOH}$$

$$\text{Percent NaOH} = \frac{0.254\ \text{g}}{1.136\ \text{g}} \times 100 = 22.4\%\ \text{NaOH}$$

Hydrochloric acid and sodium hydroxide react in a 1/1 mole ratio. But titrations can also be considered when the reaction is in a different mole ratio. For example, if a standard solution of NaOH is used to neutralize sulfuric acid, H_2SO_4, the reaction is

$$\underbrace{2H^+ + SO_4^{2-}}_{\textbf{Sulfuric acid}} + \underbrace{2(Na^+ + OH^-)}_{\textbf{Sodium hydroxide}} \rightarrow 2H_2O + 2Na^+ + SO_4^{2-} \qquad (25.6.7)$$

From this reaction it is seen that there are 2 moles NaOH reacting for each mole H_2SO_4 so

$$\text{moles NaOH} = 2 \times (\text{moles } H_2SO_4) \qquad (25.6.8)$$

Therefore, the relationship between the molar concentration of a sulfuric acid solution, its volume, the molar concentration of an NaOH solution used to neutralize the H_2SO_4 and its volume is

$$M_{NaOH} \times \text{volume NaOH} = 2 \times (M_{H_2SO_4} \times \text{volume } H_2SO_4) \qquad (25.6.9)$$

Several different kinds of reactions other than acid-base reactions can be used for titrations. The oldest titration is a precipitation titration of chloride with silver nitrate, the Mohr method dating from 1856:

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$$Ag^{+}(aq) + NO_3^{-}(aq) + Cl^{-}(aq) \rightarrow AgCl(s) + NO_3^{-} \quad (25.6.10)$$

Chromate ion, CrO_4^{2-}, is added to the mixture to indicate the end point. When excess Ag^{+} is added beyond the end point, red solid Ag_2CrO_4—which is more soluble than the white AgCl precipitate—begins to form, indicating that the end point has been reached.

Salts of the strong chelating agent ethylenediaminetetraacetic acid can be used to chelate metal ions in a 1/1 reaction. The chelating EDTA anion, represented Y^{4-}, reacts with metal ions being titrated, such as Ca^{2+},

$$Ca^{2+} + Y^{4-} \rightarrow CaY^{2-} \quad (25.6.11)$$

to produce the stable metal chelate, in this case CaY^{2-}. An indicator can be used that forms a colored chelate with the metal being titrated. This species is less stable than the EDTA chelate and when the last of the excess metal ion is chelated by EDTA, the metal-indicator chelate disappears and the color of the solution changes showing that the end point has been reached. The titration of calcium with EDTA has been used for decades to measure water hardness.

Another type of titration reaction that can be used for volumetric analysis is oxidation-reduction. For example, Fe^{2+} ion can be determined by its oxidation to Fe^{3+} ion by a solution of potassium permanganate, $KMnO_4$. The reaction is

$$5Fe^{2+} + 8H^{+} + MnO_4^{-} \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O \quad (25.6.12)$$

and it is self-indicating because in solution MnO_4^{-} has an intense purple color and the solution turns color when the end point is reached and a slight excess of MnO_4^{-} appears.

25.7 SPECTROPHOTOMETRIC METHODS

Up to this point, this chapter has covered classical methods of analysis based upon simple weighing and volume measurement. At an accelerating pace over recent decades, analytical chemistry has benefited from a wide array of analysis techniques that use instruments to observe a variety of phenomena that reflect kinds and concentrations of analytes. There are many such instrumental techniques. The main ones, based upon absorption or emission of electromagnetic radiation, production of electrical voltages or currents, separation and detection of small quantities of analytes (chromatography), and separation and detection of ions produced by analytes (mass spectrometry), are introduced in the remainder of this chapter. These are all **instrumental methods** of analysis. Several other techniques of analysis are introduced in Chapter 26.

Superimposed on instrumental methods of analysis since about 1980 have been an array of computerized control and data analysis techniques. Essentially all modern instruments for chemical analysis of any size are now computerized. A related development has been the miniaturization of instruments and the placing of instrument components and even whole instruments on microchips fabricated from silica, glass, or plastic.

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Absorption Spectrophotometry

Absorption spectrophotometry of light-absorbing species in solution, historically called colorimetry when visible light is absorbed, is still used for the analysis of many water, and some air, pollutants. Basically, absorption spectrophotometry consists of measuring the percent transmittance (%T) of monochromatic light passing through a light-absorbing solution as compared with the amount passing through a blank solution containing everything in the medium but the sought-for constituent (100%). The absorbance (A) is defined as the following:

$$A = \log \frac{100}{\%T} \tag{25.7.1}$$

The relationship between A and the concentration (C) of the absorbing substance is given by Beer's law:

$$A = abC \tag{25.7.2}$$

where a is the absorptivity, a wavelength-dependent parameter characteristic of the absorbing substance; b is the path length of the light through the absorbing solution; and C is the concentration of the absorbing substance. A linear relationship between A and C at constant path length indicates adherence to Beer's law. In many cases, analyses can be performed even when Beer's law is not obeyed, if a suitable calibration curve is prepared. A color-developing step usually is required in which the sought-for substance reacts to form a colored species, and in some cases a colored species is extracted into a nonaqueous solvent to provide a more intense color and a more concentrated solution.

Atomic Absorption and Emission Analyses

Atomic absorption analysis is commonly used for the determination of metals in environmental samples. This technique is based upon the absorption of monochromatic light by a cloud of atoms of the analyte metal. The monochromatic light can be produced by a source composed of the same atoms as those being analyzed. The source produces intense electromagnetic radiation with a wavelength exactly the same as that absorbed by the atoms, resulting in extremely high selectivity. The basic components of an atomic absorption instrument are shown in Figure 25.6. The key element is the hollow cathode lamp in which atoms of the analyte metal are energized such that they become electronically excited and emit radiation with a very narrow wavelength band characteristic of the metal. This radiation is guided by the appropriate optics through a flame into which the sample is aspirated. In the flame, most metallic compounds are decomposed, and the metal is reduced to the elemental state, forming a cloud of atoms. These atoms absorb a fraction of radiation in the flame. The fraction of radiation absorbed increases with the concentration of the sought-for element in the sample according to the Beer's law relationship (Eq. 25.7.2). The attenuated light beam next goes to a monochromator to eliminate extraneous light resulting from the flame, and then to a detector.

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Atomizers other than a flame can be used. The most common of these is the graphite furnace, an electrothermal atomization device that consists of a hollow graphite cylinder placed so that the light beam passes through it. A small sample of up to 100 µL is inserted in the tube through a hole in the top. An electric current is passed through the tube to heat it—gently at first to dry the sample, then rapidly to vaporize and excite the metal analyte. The absorption of metal atoms in the hollow portion of the tube is measured and recorded as a spike-shaped signal. A diagram of a graphite furnace with a typical output signal is shown in Figure 25.7. The major advantage of the graphite furnace is that it gives detection limits up to 1000 times lower than those of conventional flame devices.

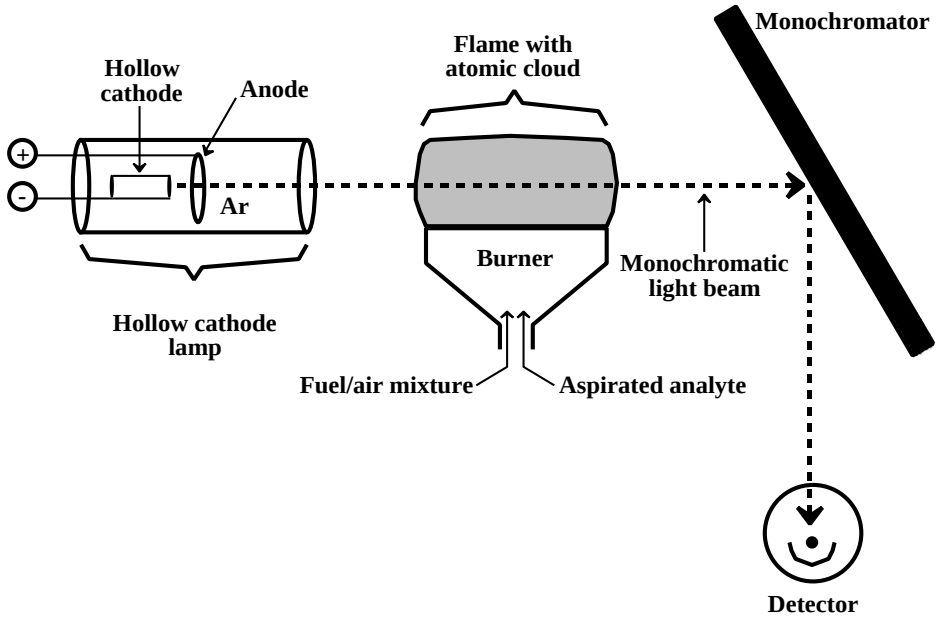


Figure 25.6 The basic components of a flame atomic absorption spectrophotometer.

A special technique for the flameless atomic absorption analysis of mercury involves room-temperature reduction of mercury to the elemental state by tin(II) chloride in solution, followed by sweeping the mercury into an absorption cell with air. Nanogram (10^{-9}g) quantities of mercury can be determined by measuring mercury absorption at 253.7 nm.

Atomic Emission Techniques

Metals can be determined in water, atmospheric particulate matter, and biological samples very well by observing the spectral lines emitted when they are heated to a very high temperature. An especially useful atomic emission technique is inductively coupled plasma atomic emission spectroscopy (ICP/AES). The "f1ame" in which analyte atoms are excited in plasma emission consists of an incandescent plasma (ionized gas) of argon heated inductively by radiofrequency energy at 4–50 MHz and 2–5 kW (Figure 25.8). A stream of ionized argon absorbs the energy from

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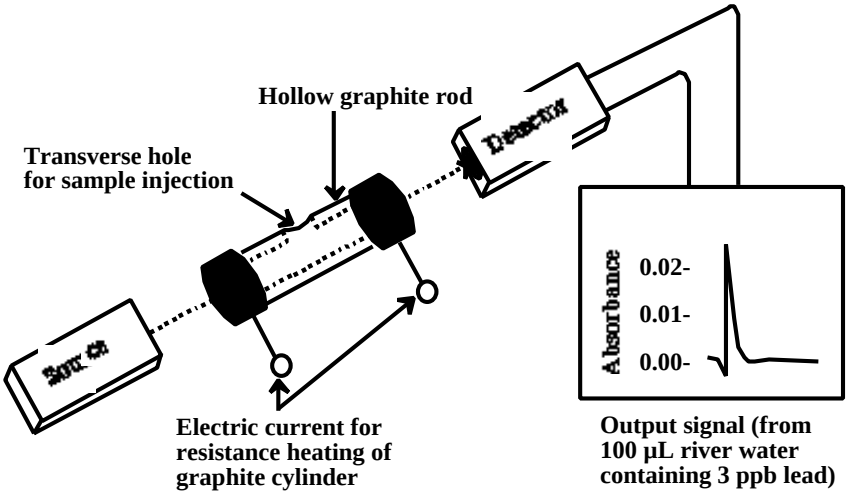


Figure 25.7 Graphite furnace for atomic absorption analysis and typical output signal.

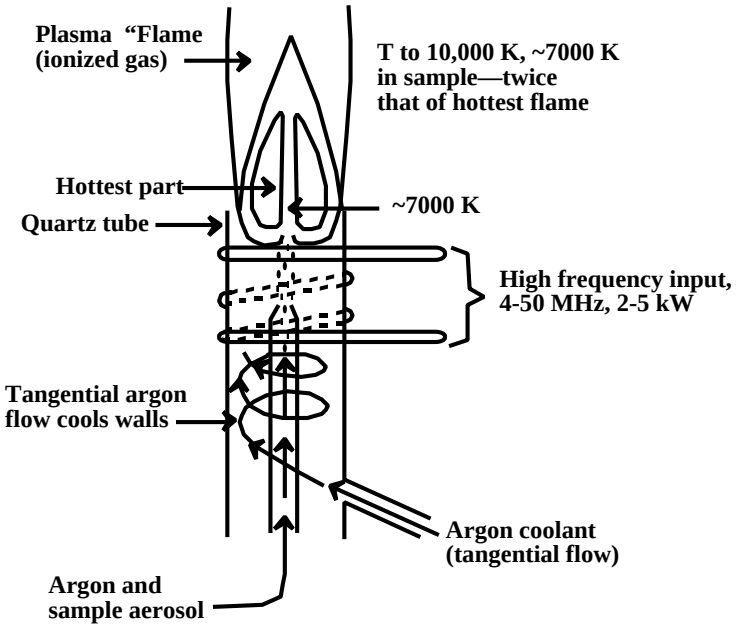


Figure 25.8 Schematic diagram showing inductively coupled plasma used for optical emission spectroscopy.

an induction coil, producing temperatures up to 10,000 K. The sample atoms are subjected to temperatures around 7000 K, twice those of the hottest conventional flames (for example, nitrous oxide-acetylene operates at 3200 K). Since emission of light increases exponentially with temperature, lower detection limits are obtained. Furthermore, the technique enables emission analysis of some of the environmentally important metalloids such as arsenic, boron, and selenium. Interfering chemical

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reactions and interactions in the plasma are minimized as compared with flames. Of greatest significance, however, is the capability of analyzing as many as 30 elements simultaneously, enabling a true multielement analysis technique. Plasma atomization combined with mass spectrometric measurement of analyte elements is a relatively new technique that is an especially powerful means for multielement analysis.

25.8 ELECTROCHEMICAL METHODS OF ANALYSIS

Several useful techniques for water analysis utilize electrochemical sensors. These techniques can be potentiometric, voltammetric, or amperometric. Potentiometry is based upon the general principle that the relationship between the potential of a measuring electrode and that of a reference electrode is a function of the log of the activity of an ion in solution. For a measuring electrode responding selectively to a particular ion, this relationship is given by the Nernst equation,

$$E = E^o + \frac{2.303RT}{zF} \log(a_z) \qquad (25.8.1)$$

where E is the measured potential; E^o is the standard electrode potential; R is the gas constant; T is the absolute temperature; z is the signed charge (+ for cations, - for anions); *F* is the Faraday constant; and a is the activity of the ion being measured. At a given temperature, the quantity 2.303RT/*F* has a constant value; at 25°C it is 0.0592 volt (59.2 mv). At constant ionic strength, the activity, a, is directly proportional to concentration, and the Nernst equation can be written as the following for electrodes responding to Cd^{2+} and F^-, respectively:

$$E \text{ (in mv)} = E^o + \frac{59.2}{2} \log [Cd^{2+}] \qquad (25.8.2)$$

$$E = E^o - 59.2 \log [F^-] \qquad (25.8.3)$$

Electrodes that respond more or less selectively to various ions are called **ion-selective electrodes**. Generally, the potential-developing component is a membrane of some kind that allows for selective exchange of the sought-for ion. The glass electrode used for the measurement of hydrogen-ion activity and pH is the oldest and most widely used ion-selective electrode. The potential is developed at a glass membrane that selectively exchanges hydrogen ion in preference to other cations, giving a Nernstian response to hydrogen ion activity, a_{H^+}:

$$E = E^o + 59.2 \log(a_{H^+}) \qquad (25.8.4)$$

Of the ion-selective electrodes other than glass electrodes, the fluoride electrode is the most successful. It is well-behaved, relatively free of interferences, and has an adequately low detection limit and a long range of linear response. Like all ion-selective electrodes, its electrical output is in the form of a potential signal that is proportional to log of concentration. A small error in E leads to a variation in log of concentration, which leads to relatively high concentration errors.

Voltammetric techniques, the measurement of current resulting from potential applied to a microelectrode, have found some applications in water analysis. One

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such technique is differential-pulse polarography, in which the potential is applied to the microelectrode in the form of small pulses superimposed on a linearly increasing potential. The current is read near the end of the voltage pulse and compared with the current just before the pulse was applied. It has the advantage of minimizing the capacitive current from charging the microelectrode surface, which sometimes obscures the current due to the reduction or oxidation of the species being analyzed. Anodic-stripping voltammetry involves deposition of metals on an electrode surface over a period of several minutes followed by stripping them off very rapidly using a linear anodic sweep. The electrodeposition concentrates the metals on the electrode surface, and increased sensitivity results. An even better technique is to strip the metals off using a differential pulse signal. A differential-pulse anodic-stripping voltammogram of copper, lead, cadmium, and zinc in tap water is shown in Figure 25.9.

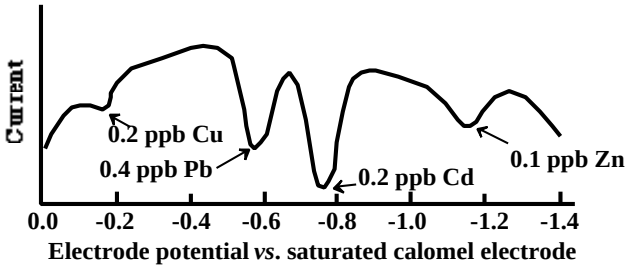


Figure 25.9 Differential-pulse anodic-stripping voltammogram of tap water at a mercury-plated, wax-impregnated graphite electrode.

25.9 CHROMATOGRAPHY

First described in the literature in the early 1950s, gas chromatography has played an essential role in the analysis of organic materials. Gas chromatography is both a qualitative and quantitative technique; for some analytical applications of environmental importance, it is remarkably sensitive and selective. Gas chromatography is based upon the principle that when a mixture of volatile materials transported by a carrier gas is passed through a column containing an adsorbent solid phase or, more commonly, an absorbing liquid phase coated on a solid material, each volatile component will be partitioned between the carrier gas and the solid or liquid. The length of time required for the volatile component to traverse the column is proportional to the degree to which it is retained by the nongaseous phase. Since different components may be retained to different degrees, they will emerge from the end of the column at different times. If a suitable detector is available, the time at which the component emerges from the column and the quantity of the component are both measured. A recorder trace of the detector response appears as peaks of different sizes, depending upon the quantity of material producing the detector response. Both quantitative and (within limits) qualitative analyses of the sought-for substances are obtained.

The essential features of a gas chromatograph are shown schematically in Figure 25.10. The carrier gas generally is argon, helium, hydrogen, or nitrogen. The sample

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is injected as a single compact plug into the carrier gas stream immediately ahead of the column entrance. If the sample is liquid, the injection chamber is heated to vaporize the liquid rapidly. The separation column may consist of a metal or glass tube packed with an inert solid of high surface area covered with a liquid phase, or it may consist of an active solid, which enables the separation to occur. More commonly, capillary columns are now employed that consist of very small-diameter, very long tubes in which the liquid phase is coated on the inside of the column.

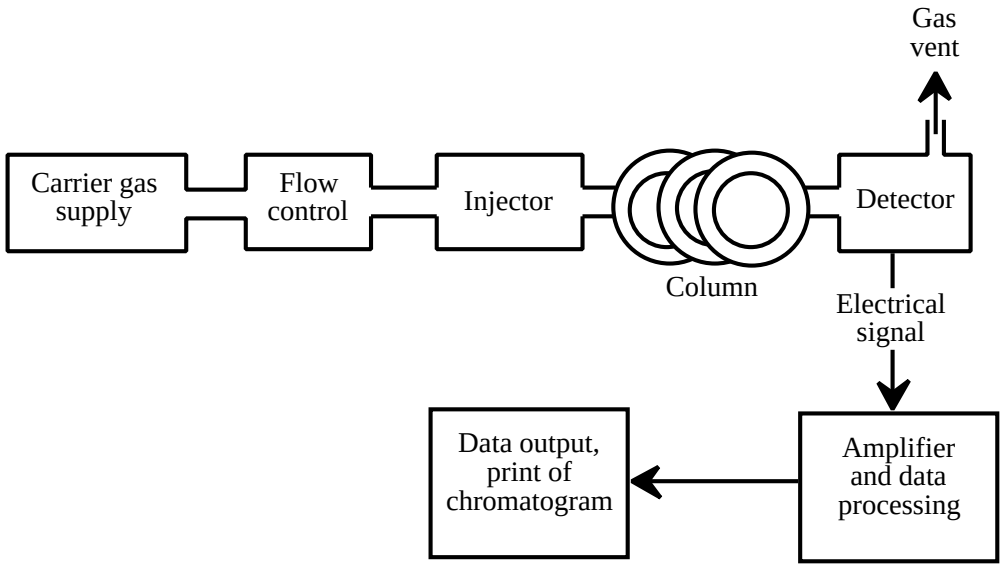


Figure 25.10 Schematic diagram of the essential features of a gas chromatograph.

The component that primarily determines the sensitivity of gas chromatographic analysis and, for some classes of compounds, the selectivity as well, is the detector. One such device is the thermal conductivity detector, which responds to changes in the thermal conductivity of gases passing over it. The electron-capture detector, which is especially useful for halogenated hydrocarbons and phosphorus compounds, operates through the capture of electrons emitted by a beta-particle source. The flame-ionization gas chromatographic detector is very sensitive for the detection of organic compounds. It is based upon the phenomenon by which organic compounds form highly conducting fragments, such as C^+, in a flame. Application of a potential gradient across the flame results in a small current that can be readily measured. The mass spectrometer, described in Section 25.10, can be used as a detector for a gas chromatograph. A combined gas chromatograph/mass spectrometer (GC/MS) instrument is an especially powerful analytical tool for organic compounds.

Gas chromatographic analysis requires that a compound exhibit at least a few mm of vapor pressure at the highest temperature at which it is stable. In many cases, organic compounds that cannot be passed through a chromatographic column directly can be converted to derivatives that are amenable to gas chromatographic analysis. It is seldom possible to analyze organic compounds in water by direct

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injection of the water into the gas chromatograph; higher concentration is usually required. Two techniques commonly employed to remove volatile compounds from water and concentrate them are (1) extraction with solvents and (2) purging volatile compounds with a gas, such as helium; concentrating the purged gases on a short column; and driving them off by heat into the chromatograph.

High-Performance Liquid Chromatography

A liquid mobile phase used with very small column-packing particles enables high-resolution chromatographic separation of materials in the liquid phase. Very high pressures up to several thousand psi are required to get a reasonable flow rate in such systems. Analysis using such devices is called **high-performance liquid chromatography** (HPLC) and offers an enormous advantage in that the materials analyzed need not be changed to the vapor phase, a step that often requires preparation of a volatile derivative or results in decomposition of the sample. The basic features of a high-performance liquid chromatograph are the same as those of a gas chromatograph, shown in Figure 25.10, except that a solvent reservoir and high-pressure pump are substituted for the carrier gas source and regulator. A hypothetical HPLC chromatogram is shown in Figure 25.11. Refractive index and ultraviolet detectors are both used for the detection of peaks coming from the liquid chromatograph column. Fluorescence detection can be especially sensitive for some classes of compounds. Mass spectrometric detection of HPLC effluents has led to the development of LC/MS analysis. Somewhat difficult in practice, this technique can be a powerful tool for the determination of analytes that cannot be subjected to gas chromatography. High-performance liquid chromatography has emerged as a very useful technique for the analysis of a number of water pollutants.

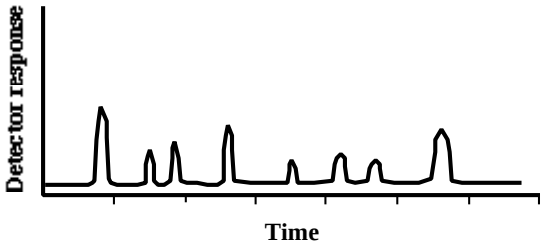


Figure 25.11 Hypothetical HPLC chromatogram.

25.10 MASS SPECTROMETRY

Mass spectrometry is particularly useful for the identification of specific organic pollutants. It depends upon the production of ions by an electrical discharge or chemical process, followed by separation based on the charge-to-mass ratio and measurement of the ions produced. The output of a mass spectrometer is a mass spectrum, such as the one shown in Figure 25.12. A mass spectrum is characteristic of a compound and serves to identify it. Computerized data banks for mass spectra have been established and are stored in computers interfaced with mass spectrometers. Identification of a mass spectrum depends upon the purity of the compound from which the spectrum is taken. Prior separation by gas

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chromatography with continual sampling of the column effluent by a mass spectrometer, commonly called gas chromatography-mass spectrometry (GC/MS), is particularly effective in the analysis of organic pollutants.

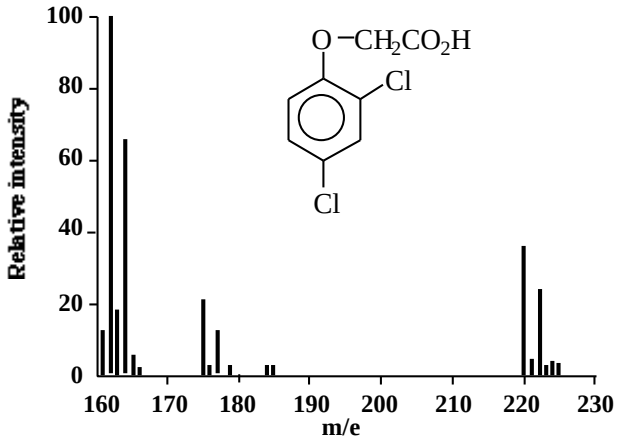


Figure 25.12 Partial mass spectrum of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D), a common water pollutant.

25.11 AUTOMATED ANALYSES

Huge numbers of analyses must often be performed to get meaningful results and for reasons of economics. This has resulted in the development of a number of automated procedures in which traditional "wet chemical" methods of analysis have been adopted to automated procedures. With such procedures, the samples are introduced through a sampler and the analyses performed and results posted without manual manipulation of reagents and apparatus. Such procedures have been developed and instruments marketed for the determination of a number of analytes. In water, automated analyses have been developed from wet chemical procedures for alkalinity, sulfate, ammonia, nitrate/nitrite, and metals. The somewhat cumbersome West-Gaeke determination of sulfur dioxide in air has been adapted to automated analyzers. Colorimetric procedures are popular for such automated analytical instruments, using simple, rugged colorimeters for absorbance measurements.

Figure 25.13 shows an automated analytical system for the determination of water alkalinity. The reagents and sample liquids are transported through the analyzer by a peristaltic pump. This relatively simple device consists basically of rollers moving over flexible tubing, which "squeezes" solutions through the tubing. By using different sizes of tubing and varying the speed of the rollers, the flow rates of the reagents are proportioned. Air bubbles are introduced into the liquid stream to aid mixing and to separate one sample from another. Mixing of the sample and various reagents is accomplished in mixing coils. Since many color-developing reactions are not rapid, a delay coil is provided that allows the color to develop before reaching the colorimeter. Bubbles are removed from the liquid stream by a debubbler pror to introduction into the flowcell for colorimetric analysis.

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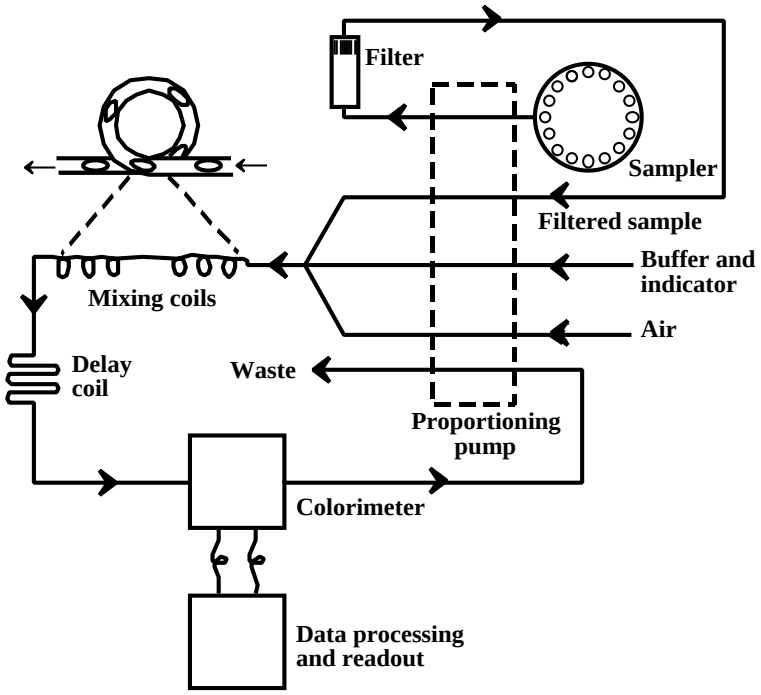


Figure 25.13 Automated analyzer system for the determination of total alkalinity in water. Addition of a water sample to a methyl orange solution buffered to pH 3.1 causes a loss of color in proportion to the alkalinity in the sample.

25.12 IMMUNOASSAY SCREENING

Immunoassay has emerged as a useful technique for screening samples, such as hazardous-waste residues, for specific kinds of pollutants. Commercial immunoassay techniques have been developed that permit very rapid analyses of large numbers of samples. A variety of immunoassay techniques have been developed. These techniques all use biologically produced antibodies that bind specifically to analytes or classes of analytes. This binding is combined with chemical processes that enable detection through a signal-producing species (reporter reagent) such as enzymes, chromophores, fluorophores, and luminescent compounds. The reporter reagent binds with the antibody. When an analyte is added to the antibody to displace the reagent, the concentration of displaced reagent is proportional to the level of analyte displacing it from the antibody. Detection of the displaced reporter reagent enables quantification of the analyte.

Immunoassay techniques are divided into the two major categories of heterogeneous and homogeneous; the former requires a separation (washing) step, whereas the latter does not require such a step. Typically, when heterogeneous procedures are used, the antibody is immobilized on a solid support on the inner surface of a disposable test tube. The sample is contacted with the antibody displacing reporter reagent, which is removed by washing. The amount of reagent displaced, commonly

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measured spectrophotometrically, is proportional to the amount of analyte added. Very widely used enzyme immunoassays make use of reporter reagent molecules bound with enzymes, and kits are available for enzyme-linked immunosorbent assays (ELISA) of a number of organic species likely to be found in hazardous wastes.

Immunoassay techniques have been approved for the determination of numerous analytes commonly found in hazardous wastes. Where the EPA method numbers are given in parentheses, these include pentachlorophenol (4010), 2,4-dichlorophenoxyacetic acid (4015), polychlorinated biphenyls (4020), petroleum hydrocarbons (4030), polycyclic aromatic hydrocarbons (4035), toxaphene (4040), chlordane (4041), DDT (4042), TNT explosives in soil (4050), and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in soil (4051). Enzyme-linked immunosorbent assays have been reported for monitoring pentachlorophenol, BTEX (benzene, toluene, ethylbenzene, and *o*-, *m*-, and *p*-xylene) in industrial effluents.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

In performing chemical analysis, a [1]_____ is performed to determine *what* is in a sample. The amount, concentration, composition, or percent of a substance present is determined by [2]_____. The major steps involved in the chemical analysis process are [3]_____ _____ _____. The first step in the analytical process is to obtain [4]_____. Sample processing is performed to [5]_____ _____. Based upon whether a sample is retained essentially in its original form, chemical analyses can be divided into the two categories of [6]_____. After sample processing, it is often necessary to eliminate [7]_____. The substance that is measured in a chemical analysis is the [8]_____, the specific measurement of this substance is referred to as a [9]_____, whereas the total process to which the sample is subjected is called [10]_____. Both qualitative and quantitative analysis are divided between [11]_____ methods involving primarily chemical reactions and simple measurements of mass and volume and [12]_____ that use instruments of varying degress of complexity and sophistication to measure quantities of analyte. Classical methods are often [13]_____ procedures using reagents in solution and reactions of dissolved analyte. The actual measurements involved in a chemical analysis can be divided into the two major categories of [14]_____ _____. The degree to which numbers in a group of analytical results are in agreement with each other is the [15]_____ of the group of numbers, a lack of which may indicate the presence of [16]_____ _____. [17]_____ errors vary randomly in direction

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and magnitude and are from sources that [18]_____. [19]_____ errors always have a definite cause and are in the same direction. The extent to which the data or the average value of a set of data agree with the true value being determined is the [20]_____ of the data. Since a buret can be read to 0.01 mL, a volume of 36.27 mL read from a buret implies that the volume is between [21]____ and [22]____ mL. Dividing the absolute uncertainty of a number by the value being expressed gives the [23]_____. A conceptually simple means of quantitative analysis that consists of weighing samples, analytes and products of analytes is [24]_____. A precipitate is often collected for weighing in a [25]_____. The organic compound 8-hydroxyquinoline is useful as [26]_____ in the gravimetric analysis of metals. Other than gravimetric analysis, the other major type of classical "wet chemical" analysis technique is [27]_____ which consists of [28]_____ _____. The major aspects of this analytical procedure are [29]_____ _____ _____ _____ _____.

For the titration of an acid with a standard base, a plot of pH versus volume of added base titrant is a [30]_____. When a particular volume of a solution of an acid with one ionizable H per formula unit reacts with a base with one hydroxide per formula unit contained in a specified volume of base solution, the basic stoichiometric equation used that applies is [31]_____ _____. Other than acid-base reactions, titration reactions include [32]_____ _____ reactions. When titration with standard HCl is used to determine the mass of NaOH in a solid sample containing inert material along with the HCl, the equation used for the calculation is [33]_____.

In terms of percent transmittance in absorption spectrometry, absorbance, A, is given by the equation [34]_____. The relationship between the absorbance and the concentration of absorbing substance is called [35]_____ expressed mathematically as [36]_____. The principle of atomic absorption analysis is the [37]_____ by a [38]_____.

Often much lower detection limits can be determined by atomic absorption by using a device known as a [39]_____. A special technique of flameless atomic absorption analysis uses a cloud of "cold" atoms for the determination of the metal [40]_____. An atomic emission technique for elemental analysis that uses a particularly hot "flame" is [41]_____ _____.

Electrochemical methods of analysis may belong to the categories of [42]_____ _____. Ion-selective electrodes produce an electrical [43]_____ in response to various kinds of ions. Gas chromatography is based upon the principle that when a mixture of volatile materials transported by a carrier gas is passed through a [44]_____ that has the ability to retain analytes to varying degrees, different analytes come out at [45]_____ and appear as [46]_____ on a recorder trace. The

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essential features of a gas chromatograph are [47]_____ _____ _____.
A chromatography system that uses a liquid mobile phase under very high pressure is called [48]_____.
A mass spectrum is [49]_____ of a compound and serves to [50]_____. The reagents and sample liquids are transported through an automated analyzer by a [51]_____ and [52]_____ are introduced into the liquid stream to aid mixing and to separate one sample from another. Immunoassay techniques of analysis use biologically produced [53]_____ _____ that act by [54]_____ _____.

Answers to Chapter Summary

1. qualitative analysis
2. quantitative analysis
3. (1) obtaining and preserving a representative sample, (2) sample processing, (3) measurement of analyte quantity, and (4) calculating results
4. a representative sample
5. get the sample into a form that can be analyzed
6. destructive and nondestructive
7. interferences
8. analyte
9. determination
10. an analysis
11. classical
12. instrumental methods
13. wet chemical
14. chemical and physical methods
15. precision
16. indeterminate, or random, errors
17. Indeterminate
18. cannot be determined
19. Determinate
20. accuracy
21. 36.26
21. 36.28
23. relative uncertainty
24. gravimetric analysis
25. filter crucible
26. an organic precipitant
27. titration
28. measuring the volume of a reagent required to react with an analyte
29. a measured quantity of sample is taken, a standard solution of standard solution is reacted with analyte, and indicator is used to show end point, and the quantity or concentration of analyte are calculated

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30. titration curve
31. (volume acid) × M_{acid} = (volume base) × M_{base}
32. precipitation, chelation, and oxidation-reduction
33. $$\frac{\text{Mass NaOH}}{\text{molar mass NaOH}} = (\text{Volume HCl}) \times M_{HCl}$$
34. $$A = \log \frac{100}{\%T}$$
35. Beer's law
36. A = abc
37. absorption of light
38. cloud of atoms
39. graphite furnace atomizer
40. mercury
41. inductively coupled plasma atomic emission spectroscopy (ICP/AES)
42. potentiometric, voltammetric, or amperometric
43. potential
44. column
45. different times
46. peaks
47. carrier gas supply, flow control, injector, column, detector, and amplifier for the signal from the detector
48. high-performance liquid chromatography
49. characteristic
50. identify it
51. peristaltic pump
52. air bubbles
53. antibodies
54. binding specifically to analytes or classes of analytes

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QUESTIONS AND PROBLEMS

1. What is the general term applied to a constituent determined in a sample?
2. Mass and volume are the two parameters most generally measured in a chemical or wet chemical method of analysis. What two broad categories of analysis do these two measurements represent?
3. Match the following:

A. Representative sample	1.Must be removed or chemically sequestered to avoid affecting the determination
B. Sample processing	2.Actual process of finding out how much of an analyte is present
C. Interferences	3.Usually involves putting the sample into solution
D. Determination	4.Ideally should have a composition the same as that of the material whose composition is to be determined

4. Mass and volume are the two parameters most generally measured in a chemical or wet chemical method of analysis. What two broad categories of analysis do these two measurements represent?
5. The heat released per unit mass of coal was determined for the coal in a unit train containing 10,000 metric tons of coal. A representative sample was obtained by "grab sampling" 64 approximately 1-kg portions of coal from the train. These were reduced to three 1-g samples, for which the heat content was determined and the average taken. What percentage of the total coal in the train was taken for analysis?
6. What mass of $BaSO_4$, molar mass 233.4, can be precipitated from a solution containing 1.538 g of $Fe_2(SO_4)_3$, molar mass 399.9, by the addition of excess $BaCl_2$?
7. What mass of Fe_2O_3, molar mass 159.7, can be obtained by the reaction of 0.948 g of pure Fe, molar mass 55.8?

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8. The chemical analysis of a sample of lake water for dissolved O_2 showed 0.668 mg of O_2 dissolved in a 75.0 mL sample of the water. What was the molar concentration of O_2 in the water?

9. A 25.00 mL sample of an industrial water stream containing Na_2CO_3 required 32.60 mL of a 0.1104 M solution of standard HCl to react with the Na_2CO_3 according to the reaction

 $$2HCl + Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2$$

 What was the concentration of Na_2CO_3 in the solution in units of mg/L?

10. Define titrant.

11. Describe the general characteristics of a titration curve for the titration of HCl with NaOH.

12. How is the end point found in the titration of HCl with NaOH using either a titration curve or an indicator?

13. A 3.471-g sample of a compound containing C, H, and O was ignited in a stream of O_2 and the CO_2 and H_2O were collected. Masses of 8.758 g of CO_2 and 1.537 g of H_2O were collected. Calculate the percentages of C and H in the compound.

14. A fertilizer sample weighing 0.6379 g was dissolved and treated with $NaClO_4$ solution, yielding 0.3816 g of $KClO_4$. What was the percentage of K in the fertilizer sample?

15. A corrosion product scraped from the surface of a lightweight metal alloy was analyzed to determine the percentage of $MgCO_3$ in the product by precipitation of magnesium ammonium phosphate and ignition to $Mg_2P_2O_7$. A 0.5626-g sample of the corrosion product yielded 0.3982 g of $Mg_2P_2O_7$. What was the percentage of $MgCO_3$ in the sample?

16. Calcium ion, Ca^{2+}, reacts with the chelating titrant EDTA, as shown in Reaction 25.6.11, whereas sodium ion, Na^+, does not react with EDTA. A 0.327-g portion of a caustic mixture of solid $Ca(OH)_2$, molar mass 74.1 g/mol, and Na_2CO_3 was dissolved and titrated with 0.0917 M EDTA, requiring 33.8 mL of the EDTA solution to reach the end point. What was the percentage of $Ca(OH)_2$ in the mixture?

17. How many mL of a 0.0500 M solution of $KMnO_4$ acting as an oxidizing titrant would be required to react with all the Fe^{2+} ion produced by dissolving 0.623 g of a sample that is 36.2 % FeO, molar mass 71.9 g/mol, mixed with inert material?

18. Based upon material covered elsewhere in the book regarding the nature of electrons in atoms, quantum chemistry, and photochemistry, attempt to explain the phenomena of atomic absorption and atomic emission discussed as analytical techniques in this chapter.

19. In reference to Equation 25.8.4, calculate the voltage change at a glass electrode used to measure pH for each unit change in pH.

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20. Distinguish among the electron-capture detector, flame-ionization detector, and mass spectrometer as detectors for gas chromatographic separations.
21. What is required to get a reasonable flow rate in a high performance liquid chromatographic separation?
22. What is the basis of separations made in mass spectrometry? Why is mass spectrometry one of the most specific means of detecting organic compounds?
23. What are the main components of an automated analyzer system? What are the functions of each?
24. What is the basis of immunoassay analysis? What is meant by its being classified as a good screening technique?
25. A sample of a colored analyte at a concentration of 3.60×10^{-3} mol/L shows 34.2 percent transmittance in a 2.00 cm cell. What is the value of a in the Beer's law equation for this substance at the wavelength measured? If a sample of the colored analyte of unknown concentration gives an absorbance, A, of 0.520 in the same cell at the same wavelength, what is the concentration of the analyte in this solution?

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26 ENVIRONMENTAL AND XENOBIOTICS ANALYSIS

26.1 INTRODUCTION TO ENVIRONMENTAL CHEMICAL ANALYSIS

Scientists' understanding of the environment can only be as good as their knowledge of the identities and quantities of pollutants and other chemical species in water, air, soil, and biological systems. Therefore, proven, state-of-the-art techniques of chemical analysis, properly employed, are essential to environmental chemistry. Now is a very exciting period in the evolution of analytical chemistry, characterized by the development of new and improved analysis techniques that enable detection of much lower levels of chemical species and a vastly increased data throughput. These developments pose some challenges. Because of the lower detection limits of some instruments, it is now possible to see quantities of pollutants that would have escaped detection previously, resulting in difficult questions regarding the setting of maximum allowable limits of various pollutants. The increased output of data from automated instruments has in many cases overwhelmed human capacity to assimilate and understand it.

Challenging problems still remain in developing and utilizing techniques of environmental chemical analysis. Not the least of these problems is knowing which species should be measured, or even whether an analysis should be performed at all. The quality and choice of analyses is much more important than the number of analyses performed. Indeed, a persuasive argument can be made that, given modern capabilities in analytical chemistry, too many analyses of environmental samples are performed, whereas fewer, more carefully planned analyses would yield more-useful information.

This chapter covers some of the general aspects of environmental chemical analysis. Environmental chemical analysis can be subdivided into several overlapping categories. These include analysis of water and wastewater, analysis of wastes and solids, air and gas analysis, and analysis of biological materials and xenobiotic substances, all addressed briefly in this chapter.

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26.2 ANALYSIS OF WATER SAMPLES

Physical Properties Measured in Water

The commonly determined physical properties of water are color, residue (solids), odor, temperature, specific conductance, and turbidity. Most of these terms are self-explanatory and will not be discussed in detail. All of these properties either influence or reflect the chemistry of the water. Solids, for example, arise from chemical substances either suspended or dissolved in the water and are classified physically as total, filterable, nonfilterable, or volatile. Specific conductance is a measure of the degree to which water conducts alternating current and reflects, therefore, the total concentration of dissolved ionic material. By necessity, some physical properties must be measured in the water without sampling (see discussion of water sampling below).

Water Sampling

It is beyond the scope of this text to describe water sampling procedures in detail. It must be emphasized, however, that the acquisition of meaningful data demands that correct sampling and storage procedures be used. These procedures can be quite different for various species in water. In general, separate samples must be collected for chemical and biological analysis because the sampling and preservation techniques differ significantly. Usually, the shorter the time interval between sample collection and analysis, the more accurate the analysis will be. Indeed, some analyses must be performed in the field within minutes of sample collection. Others, such as the determination of temperature, must be done on the body of water itself. Within a few minutes after collection, water pH may change, dissolved gases (oxygen, carbon dioxide, hydrogen sulfide, chlorine) may be lost, or other gases (oxygen, carbon dioxide) may be absorbed from the atmosphere. Therefore, analyses of temperature, pH, and dissolved gases should always be performed in the field. Furthermore, precipitation of calcium carbonate accompanies changes in the pH-alkalinity-calcium carbonate relationship following sample collection. Analysis of a sample after standing may thus give erroneously low values for calcium and total hardness.

Oxidation-reduction reactions can cause substantial errors in analysis. For example, soluble iron(II) and manganese(II) are oxidized to insoluble iron(III) and manganese(IV) compounds when an anaerobic water sample is exposed to atmospheric oxygen. Microbial activity can decrease phenol or biological oxygen demand (BOD) values, change the nitrate-nitrite-ammonia balance, or alter the relative proportions of sulfate and sulfide. Iodide and cyanide frequently are oxidized. Chromium(VI) in solution may be reduced to insoluble chromium(III). Sodium, silicate, and boron are leached from glass container walls.

Samples can be divided into two major categories. **Grab samples** are taken at a single time and in a single place. Therefore, they are very specific with respect to time and location. **Composite samples** are collected over an extended time and may encompass different locations as well. In principle, the average results from a large number of grab samples give the same information as a composite sample. A com-

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posite sample has the advantage of providing an overall picture from only one analysis. On the other hand, it may miss extreme concentrations and important variations that occur over time and space.

Solid-Phase Extractors

The ease and effectiveness of various kinds of solid-phase devices for water sampling is steadily increasing their use in water analysis. Based upon size and physical configuration, at least three categories of such devices are available. One of these is the conventional solid-phase extractor (SPE) containing an extracting solid in a column. Activated carbon has been used for decades for this purpose, but synthetic materials, such as those composed of long hydrocarbon chains (C18) bound to solids have been found to be quite useful. A typical procedure uses a polymer-divinylstyrene extraction column to remove pesticides from water. The pesticide analytes are eluted from the SPE with ethyl acetate and measured by gas chromatography. A mean recovery of 85% has been reported.

Solid-phase microextraction (SPME) devices constitute a second kind of solid-phase extractor. These make use of very small-diameter devices in which analytes are bonded directly to the extractor walls, then eluted directly into a chromatograph. The use of SPME devices for the determination of haloethers in water has been described.

A third kind of device, disks composed of substances that bind with and remove analytes from water when the water is filtered through them, are available for a number of classes of substances and are gaining in popularity because of their simplicity and convenience. As an example, solid phase extraction disks can be used to remove and concentrate radionuclides from water, including ^{99}Tc, ^{137}Cs, ^{90}Sr, ^{238}Pu. Organic materials sampled from water with such disks include haloacetic acids and acidic and neutral herbicides.

Water Sample Preservation

It is not possible to completely protect a water sample from changes in composition. However, various additives and treatment techniques can be employed to minimize sample deterioration. These methods are summarized in Table 26.1.

The most general method of sample preservation is refrigeration to 4°C. Freezing normally should be avoided because of physical changes—formation of precipitates and loss of gas—that can adversely affect sample composition. Acidification is commonly applied to metal samples to prevent their precipitation, and it also slows microbial action. In the case of metals, the samples should be filtered before adding acid to enable determination of dissolved metals. Sample holding times vary, from zero for parameters such as temperature or dissolved oxygen measured by a probe, to 6 months for metals. Many different kinds of samples, including those to be analyzed for acidity, alkalinity, and various forms of nitrogen or phosphorus, should not be held for more than 24 hours. Details on water sample preservation are to be found in standard references on water analysis, such as those listed at the end of this chapter. Instructions should be followed for each kind of sample to ensure meaningful results.

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Table 26.1 Preservatives and Preservation Methods Used with Water Samples

Preservative or technique used	Effect on sample	Type of samples for which the method is employed
Nitric acid	Keeps metals in solution	Metal-containing samples
Sulfuric acid	Bactericide	Biodegradable samples containing organic carbon, oil, or grease
	Formation of sulfates with volatile bases	Samples containing amines or ammonia
Sodium hydroxide	Forms sodium salts from volatile acids	Samples containing volatile organic acids or cyanides
Chemical reaction	Fix a particular constituent	Samples to be analyzed for dissolved oxygen using the Winkler method

26.3 CLASSICAL METHODS OF WATER ANALYSIS

The most common classical methods for water analysis are titrations. Some of the titration procedures used are discussed in this section. The principles of titration analysis are discussed in Chapter 25, Section 25.6.

Acidity (see Chapter 11, Section 11.6) is determined simply by titrating hydrogen ion with base. Titration to the methyl orange endpoint (pH 4.5) yields the "free acidity" due to strong acids (HCl, H_2SO_4). Carbon dioxide does not, of course, appear in this category. Titration to the phenolphthalein endpoint, pH 8.3, yields total acidity and accounts for all acids except those weaker than HCO_3^-.

Alkalinity can be determined by titration with H_2SO_4 to pH 8.3 to neutralize bases as strong as, or stronger than, carbonate ion,

$$CO_3^{2-} + H^+ \rightarrow HCO_3^- \qquad (26.3.1)$$

or by titration to pH 4.5 to neutralize bases weaker than CO_3^{2-}, but as strong as, or stronger than, HCO_3^-:

$$HCO_3^- + H^+ \rightarrow H_2O + CO_2(g) \qquad (26.3.2)$$

Titration to the lower pH yields total alkalinity.

The ions involved in water hardness, a measure of the total concentration of calcium and magnesium in water, are readily titrated at pH 10 with a solution of EDTA, a chelating agent mentioned as a titrant for metals in Chapter 25, Section 25.6. The titration reaction is

$$Ca^{2+}(\text{or } Mg^{2+}) + H_2Y^{2-} \rightarrow CaY^{2-}(\text{or } MgY^{2-}) + 2H^+ \qquad (26.3.3)$$

where H_2Y^{2-} is the partially ionized EDTA chelating agent. Eriochrome Black T is used as an indicator, and it requires the presence of magnesium, with which it forms a wine-red complex.

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Several oxidation-reduction titrations can be used for environmental chemical analysis. Oxygen is determined in water by the Winkler titration. The first reaction in the Winkler method is the oxidation of manganese(II) to manganese(IV) by the oxygen analyte in a basic medium; this reaction is followed by acidification of the brown hydrated MnO_2 in the presence of I^- ion to release free I_2, then titration of the liberated iodine with standard thiosulfate, using starch as an endpoint indicator:

$$Mn^{2+} + 2OH^- + {}^1/_2O_2 \rightarrow MnO_2(s) + H_2O \quad (26.3.4)$$

$$MnO_2(s) + 2I^- + 4H^+ \rightarrow Mn^{2+} + I_2 + 2H_2O \quad (26.3.5)$$

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^- \quad (26.3.6)$$

A back calculation from the amount of thiosulfate required yields the original quantity of dissolved oxygen (DO) present. Biochemical oxygen demand, BOD (see Chapter 12, Section 12.9), is determined by adding a microbial "seed" to the diluted sample, saturating with air, incubating for 5 days, and determining the oxygen remaining. The results are calculated to show BOD as mg/L of O_2. A BOD of 80 mg/L, for example, means that biodegradation of the organic matter in a liter of the sample would consume 80 mg of oxygen.

26.4 INSTRUMENTAL METHODS OF WATER ANALYSIS

Absorption Spectrophotometry

Absorption spectrophotometry of light-absorbing species in solution, an instrumental technique discussed in Chapter 25, Section 25.7, is useful for a number of common analytes measured in water. Recall that absorption spectrophotometry consists of measuring the percent transmittance (%T) of monochromatic light passing through a light-absorbing solution as compared with the amount passing through a blank solution containing everything in the medium but the sought-for constituent (100%). The absorbance (A) is defined as log(100/%T) and the relationship between A and the concentration (C) of the absorbing substance is given by Beer's law:

$$A = abC \quad (26.4.1)$$

where a is the absorptivity, a wavelength-dependent parameter characteristic of the absorbing substance; b is the path length of the light through the absorbing solution; and C is the concentration of the absorbing substance.

A number of solution spectrophotometric methods have been developed and used for the determination of water pollutants. Some of these are summarized in Table 26.2.

Atomic Spectrophotometric Analysis of Water

Discussed in Section 25.7, atomic spectrometric methods are favored for the determination of most metals in water. Atomic absorption analysis has been widely employed for water analysis. Flame atomic absorption is useful for a variety of

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metals whose concentrations are not too low. Much lower detection limits can be obtained with flameless (graphite furnace) atomic absorption, a technique that, fortunately, is particularly useful for some of the more troublesome metal pollutants in water, including cadmium, lead, and chromium. Another water pollutant metal of great concern is mercury, which is measurable at very low levels by cold vapor atomic absorption from atomic mercury generated by reduction in solution.

Table 26.2 Solution Spectrophotometric Methods of Analysis for Water

Analyte	Reagent and Method
Arsenic	Reaction of arsine, AsH_3, with silver diethylthiocarbamate in pyridine, forming a red complex
Boron	Reaction with curcumin, forming red rosocyanine
Bromide	Reaction of hypobromite with phenol red to form bromphenol blue-type indicator
Cyanide	Formation of a blue dye from reaction of cyanogen chloride, CNCl, with pyridine-pyrazolone reagent, measured at 620 nm
Fluoride	Decolorization of a zirconium-dye colloidal precipitate ("lake") by formation of colorless zirconium fluoride and free dye
Nitrate and nitrite	Nitrate is reduced to nitrite, which is diazotized with sulfanilamide and coupled with N-(l-naphthyl)-ethylenediamine dihydrochloride to produce a highly colored azo dye measured at 540 nm
Phenols	Reaction with 4-aminoantipyrine at pH 10 in the presence of potassium ferricyanide, forming an antipyrine dye that is extracted into pyridine and measured at 460 nm
Phosphate	Reaction with molybdate ion to form a phosphomolybdate, which is selectively reduced to intensely colored molybdenum blue
Selenium	Reaction with diaminobenzidine, forming colored species absorbing at 420 nm
Silica	Formation of molybdosilicic acid with molybdate, followed by reduction to a heteropoly blue measured at 650 nm or 815 nm
Sulfide	Formation of methylene blue
Surfactants	Reaction with methylene blue to form blue salt
Tannin and lignin	Blue color from tungstophosphoric and molybdophosphoric acids

Atomic emission is useful for the determination of a number of metals and, in some respects, complementary to atomic absorption. Flame atomic emission can be performed with the same instrument used for atomic absorption. Inductively coupled

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plasma atomic emission analysis greatly extends the scope and speed of elemental analysis by atomic spectrometric means. A major advantage of inductively coupled plasma atomic emission analysis is its multielement capability, in which up to 30 elements can be measured at once. It can also measure some nonmetals.

Chromatographic Analysis of Water

The principles and types of chromatographic analysis are discussed in Chapter 25, Section 25.9. The versatility, the sensitivity, and, especially with mass spectrometric detection, the specificity of chromatographic analysis, have made various chromatographic methods favored techniques for a variety of organic analytes in water. In addition, the development of ion chromatography, discussed later in this section, has made chromatography a feasible method for measuring some important ions, particularly anions, in water.

The U.S. Environmental Protection Agency and other agencies have developed a wide array of chromatographic analysis techniques for solutes in water. These are listed according to method numbers. These techniques have been adapted to other kinds of samples as well, particularly hazardous-waste materials. Some of the major standard chromatographic techniques for the determination of analytes in water are listed in Table 26.3.

Ion Chromatography

The liquid chromatographic determination of ions, particularly anions, has enabled the measurement of species that, despite their widespread occurrence in water, used to pose special challenges for water chemists to determine. This technique has come to be known as **ion chromatography**, and its development has been facilitated by special detection techniques using so-called suppressors to enable detection of analyte ions in the chromatographic effluent. Ion chromatography has been developed for the determination of most of the common anions, including arsenate, arsenite, borate, carbonate, chlorate, chlorite, cyanide, the halides, hypochlorite, hypophosphite, nitrate, nitrite, phosphate, phosphite, pyrophosphate, selenate, selenite, sulfate, sulfite, sulfide, trimetaphosphate, and tripolyphosphate. Cations, including the common metal ions, can also be determined by ion chromatography, although they are relatively easy to determine by other means.

Total Organic Carbon in Water

The importance and possible detrimental effects of dissolved organic compounds in water were discussed in Chapter 12. Dissolved organic carbon exerts an oxygen demand in water, often is in the form of toxic substances, and is a general indicator of water pollution. Therefore, its measurement is quite important. The measurement of total organic carbon, TOC, is now recognized as the best means of assessing the organic content of a water sample. The measurement of this parameter has been facilitated by the development of methods which, for the most part, totally oxidize the dissolved organic material to produce carbon doxide. The amount of carbon dioxide evolved is taken as a measure of TOC.

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Table 26.3 Chromatography-based EPA Methods for Organic Compounds in Water

Class of compounds	Method Number GC[1]	GC/MS[2]	HPLC[3]	Example analytes
Purgeable halocarbons	601			Carbon tetrachloride
Purgeable aromatics	602			Toluene
Acrolein and acrylonitrile	603			Acrolein
Phenols	604			Phenol and chlorophenols
Benzidines			605	Benzidine
Phthalate esters	606			Bis(2-ethylhexylphthalate)
Nitrosamines	607			N-nitroso-N-dimethylamine
Organochlorine pesticides and PCBs	608			Heptachlor, PCB 1016
Nitroaromatics and isophorone	609			Nitrobenzene
Polycyclic aromatic hydrocarbons	610		610	Benzo[a]pyrene
Haloethers	611			Bis(2-chloroethyl) ether
Chlorinated hydrocarbons	612			1,3-Dichlorobenzene
2,3,7,8-Tetrachlorodibenzo-p-dioxin		613		2,3,7,8-TCDD
Organophosphorus pesticides	614			Malathion
Chlorinated Herbicides	615			Dinoseb
Triazine Pesticides	619			Atrazine
Purgeable organics		624		Ethylbenzene
Base/neutrals and acids		625		More than 70 organic compounds
Dinitro aromatic pesticides		646		Basalin (Fluchloralin)
Volatile organic compounds		1624		Vinyl chloride

[1] GC: Gas chromatography
[2] GC/MS: Gas chromatography with mass spectrometric detection
[3] HPLC: High performance liquid chromatography

TOC can be determined by a technique that uses a dissolved oxidizing agent promoted by ultraviolet light. Potassium peroxydisulfate, $K_2S_2O_8$, can be used as an oxidizing agent to be added to the sample. Phosphoric acid is also added to the sample, which is sparged with air or nitrogen to drive off CO_2 formed from HCO_3^-

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and CO_3^{2-} in solution. After sparging, the sample is pumped to a chamber containing a lamp emitting ultraviolet radiation of 184.9 nm. This radiation produces reactive free radical species such as the hydroxyl radical, HO•, discussed extensively as a photochemical reaction intermediate in Chapters 14, 15, and 16. These active species bring about the rapid oxidation of dissolved organic compounds as shown in the following general reaction:

$$\text{Organics} + HO\bullet \rightarrow CO_2 + H_2O \qquad (26.4.3)$$

After oxidation is complete, the CO_2 is sparged from the system and measured with a gas chromatographic detector or by absorption in ultrapure water followed by a conductivity measurement. Figure 26.1 is a schematic of a TOC analyzer showing the major components of this instrument.

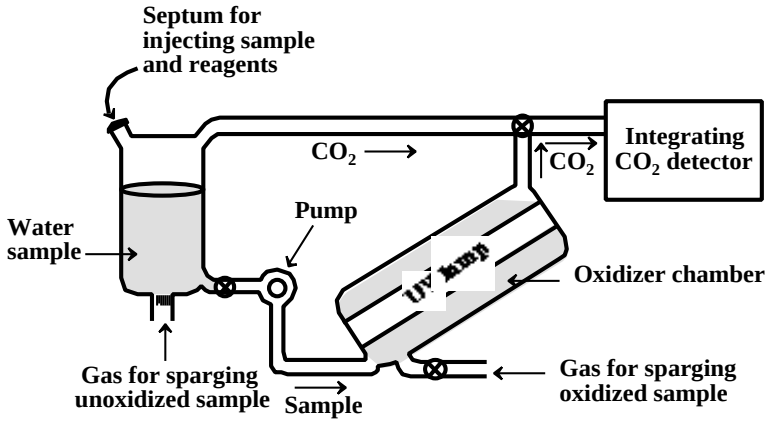


Figure 26.1 TOC analyzer employing UV-promoted sample oxidation.

Measurement of Radioactivity in Water

There are several potential sources of radioactive materials that can contaminate water (see Chapter 12, Section 12.13). Radioactive contamination of water is normally detected by measurements of gross beta and gross alpha activity, a procedure that is simpler than detecting individual isotopes. The measurement is made from a sample formed by evaporating water to a very thin layer on a small pan, which is then inserted inside an internal proportional counter. This setup is necessary because beta particles can penetrate only very thin detector windows, and alpha particles have essentially no penetrating power. More detailed information can be obtained for radionuclides that emit gamma rays by the use of gamma spectrum analysis. This technique employs solid state detectors to resolve rather closely spaced gamma peaks in the sample's spectra. In conjunction with multichannel spectrometric data analysis, it is possible to determine a number of radionuclides in the same sample without chemical separation. This method requires minimal sample preparation.

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Biological Toxins

Toxic substances produced by microorganisms are of some concern in water. Photosynthetic cyanobacteria and some kinds of algae growing in water produce potentially troublesome toxic substances. An immunoassay method of analysis (see Chapter 25, Section 25.12) for such toxins has been described.[1]

Summary of Water Analysis Procedures

The main chemical parameters commonly determined in water are summarized in Table 26.4. In addition to these, a number of other solutes, especially specific organic pollutants, may be determined in connection with specific health hazards or incidents of pollution.

26.5 ANALYSIS OF WASTES AND SOLIDS

The analysis of hazardous wastes of various kinds for a variety of potentially dangerous substances is one of the most important aspects of hazardous waste management. These analyses are performed for a number of reasons including tracing the sources of wastes, assessing the hazards posed by the wastes to surroundings and to waste remediation personnel, and determining the best means of waste treatment. Here is presented a brief overview of several of the main considerations applied to the analysis of wastes. For purposes of this discussion, wastes are broadly defined to include all kinds of solids, semisolids, sludges, liquids, contaminated soils, sediments, and other kinds of materials that are either wastes themselves or are contaminated by wastes.

For the most part, the substances determined as part of waste analysis, the *analytes*, are measured by techniques that are used for the determination of the same analytes in water and, to a lesser extent, in air. However, the preparation techniques that must be employed for waste analysis are usually more complex than those used for the same analytes in water. That is because the matrices in which the waste analytes are contained are usually relatively complicated, which makes it difficult to recover all the analytes from the waste and which introduces interfering substances. As a result, the lower limits at which substances can be measured in wastes (a parameter known as the practical quantitation limit) are usually significantly higher than in water.

There are several distinct steps in the analysis of a waste. Compared with water, wastes are often highly heterogeneous, making the collection of representative samples difficult. Whereas water samples can often be introduced into an analytical instrument with minimal preparation, the processing of hazardous wastes to get a sample that can be introduced into an instrument is often relatively complicated. Such processing can consist of dilution of oily samples with an organic solvent, extraction of organic analytes into an organic solvent, evolution and collection of volatile organic carbon analytes, or digestion of solids with strong acids and oxidants to extract metals for analysis. The products of these processes must often be subjected to relatively complicated sample cleanup procedures to remove contaminants that might interfere with the analysis or damage the analytical instrument.

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Table 26.4 Chemical Parameters Commonly Determined in Water

Chemical species	Significance in water	Methods of analysis
Acidity	Indicative of industrial pollution or acid mine drainage	Titration
Alkalinity	Water treatment, buffering, algal productivity	Titration
Aluminum	Water treatment, buffering	AA,[1] ICP[2]
Ammonia	Algal productivity, pollutant	Spectrophotometry
Arsenic	Toxic pollutant	Spectrophotometry, AA, ICP
Barium	Toxic pollutant	AA, ICP
Beryllium	Toxic pollutant	AA, ICP, fluorimetry
Boron	Toxic to plants	Spectrophotometry, ICP
Bromide	Seawater intrusion, industrial waste	Spectrophotometry, potentiometry, ion chromatography
Cadmium	Toxic pollutant	AA, ICP
Calcium	Hardness, productivity, treatment	AA, ICP, titration
Carbon dioxide	Bacterial action, corrosion	Titration, calculation
Chloride	Saline water contamination	Titration, electrochemical, ion chromatography
Chlorine	Water treatment	Spectrophotometry
Chromium	Toxic pollutant (hexavalent Cr)	AA, ICP, colorimetry
Copper	Plant growth	AA, ICP
Cyanide	Toxic pollutant	Spectrophotometry, potentiometry, ion chromatography
Fluoride	Water treatment, toxic at high levels	Spectrophotometry, potentiometry, ion chromatography
Hardness	Water quality, water treatment	AA, titration
Iodide	Seawater intrusion, industrial waste	Catalytic effect, potentiometry, ion chromatography
Iron	Water quality, water treatment	AA, ICP, colorimetry
Lead	Toxic pollutant	AA, ICP, voltammetry

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Table 26.4 (Cont.)

Lithium	May indicate some pollution	AA, ICP, flame photometry
Magnesium	Hardness	AA, ICP
Manganese	Water quality (staining)	AA, ICP
Mercury	Toxic pollutant	Flameless atomic absorption
Methane	Anaerobic bacterial action	Combustible-gas indicator
Nitrate	Algal productivity, toxicity	Spectrophotometry, ion chromatography
Nitrite	Toxic pollutant	Spectrophotometry, ion chromatography
Nitrogen (albuminoid)	Proteinaceous material	Spectrophotometry
(organic)	Organic pollution indicator	Spectrophotometry
Oil and grease	Industrial pollution	Gravimetry
Organic carbon	Organic pollution indicator	Oxidation-CO_2 measurement
Organic contaminants	Organic pollution indicator	Activated carbon adsorption
Oxygen	Water quality	Titration, electrochemical
Oxygen demand (biochemical)	Water quality and pollution	Microbiological-titration
(chemical)	Water quality and pollution	Chemical oxidation-titration
Ozone	Water treatment	Titration
Pesticides	Water pollution	Gas chromatography
pH	Water quality and pollution	Potentiometry
Phenols	Water pollution	Distillation-colorimetry
Phosphate	Productivity, pollution	Spectrophotometry
Phosphorus (hydrolyzable)	Water quality and pollution	Spectrophotometry
Potassium	Productivity, pollution	AA, ICP, flame photometry
Selenium	Toxic pollutant	Spectrophotometry, ICP, neutron activation
Silica	Water quality	Spectrophotometry, ICP
Silver	Water pollution	AA, ICP

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Table 26.4 (Cont.)

Sodium	Water quality, saltwater intrusion	AA, ICP, flame photometry
Strontium	Water quality	AA, ICP, flame photometry
Sulfate	Water quality, water pollution	Ion chromatography
Sulfide	Water quality, water pollution	Spectrophotometry, titration, chromatography
Sulfite	Water pollution, oxygen scavenger	Titration, ion chromatography
Surfactants	Water pollution	Spectrophotometry
Tannin, Lignin	Water quality, water pollution	Spectrophotometry
Vanadium	Water quality, water pollution	ICP
Zinc	Water quality, water pollution	AA, ICP

[1] AA denotes atomic absorption
[2] ICP stands for inductively coupled plasma techniques, including atomic emission and detection of plasma-atomized atoms by mass spectrometry.

Over a number of years, the U.S. Environmental Protection Agency has developed specialized methods for the characterization of wastes. These methods are given in the publication entitled *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* ("SW-846"), which is periodically updated to keep it current[2] and is available on CD/ROM.[3] Because of the difficult and exacting nature of many of the procedures in this work and because of the hazards associated with the use of reagents such as strong acids and oxidants employed for sample digestion and solvents used to extract organic analytes, anyone attempting analyses of hazardous-waste materials should use this resource and follow procedures carefully with special attention to precautions.

Sample Digestion

To analyze a solid waste sample by flame atomic absorption spectroscopy, graphite furnace absorption spectroscopy, inductively coupled argon plasma spectroscopy, or inductively coupled argon plasma mass spectrometry, the sample must first be digested to get the analyte metals in solution. Digestion dissolves only those fractions of metals that can be put into solution under relatively extreme conditions and therefore enables measurement of available metals. It should be noted that sample digestion procedures generally use highly corrosive, dangerous reagents that are strong acids and strong oxidants and demand expert personnel using the proper equipment, including fume hoods and adequate personnel protection.

EPA Method 3050 is a procedure for acid digestion of sediments, sludges, and soils. A sample of up to 2 g is treated with a mixture of nitric acid and hydrogen peroxide; the sample is then refluxed with either con. HNO_3 or con. HCl, then refluxed with dilute HCl, filtered, and the filtrate analyzed for metals.

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Microwave heating can be used to assist the digestion of samples. The procedure for the digestion of aqueous liquids consists of mixing a 45 mL sample with 5 mL of concentrated nitric acid, placing it in a fluorocarbon (Teflon) digestion vessel, and heating for 20 minutes. After digestion is complete, the sample is cooled, solids are separated by filtration or centrifugation, and the liquid remaining is analyzed by the appropriate atomic spectrometric technique.

Method 3052 is a procedure for microwave-assisted acid digestion of siliceous and organically based matrices. It can be used on a variety of kinds of samples including biological tissues, oils, oil-contaminated soils, sediments, sludges, and soil. This method is not appropriate for analyses of leachable metals, but is used for measurement of total metals. A sample of up to 0.5 g is digested with microwave heating for 15 minutes in a chemically resistant fluorocarbon polymer container in an appropriate acid mixture. Commonly, the reagents employed are a mixture of 9 mL of con. nitric acid and 3 mL hydrofluoric acid, although other acid mixtures employing reagents such as con. HCl and hydrogen peroxide can be used. The sample is heated in the microwave oven to 180˚C and held at that temperature for at least 9.5 minutes. After heating, the residual solids are filtered off and the filtrate analyzed for metals.

Many kinds of hazardous waste samples contain metals dissolved or suspended in viscous petroleum products, including oils, oil sludges, tars, waxes, paints, paint sludges, and other hydrocarbon materials. Method 3031 can be used to dissolve these metals—including antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead molybdenum, nickel, selenium, silver, thallium, vanadium, and zinc—in a form suitable for atomic spectrometric analysis. The procedure involves mixing 0.5 g of sample with 0.5 g of finely ground $KMnO_4$ and 1.0 mL of con. H_2SO_4, which causes a strongly exothermic reaction to occur as the hydrocarbon matrix is oxidized. After the reaction has subsided, 2 mL of con. HNO_3 and 2 mL of con. HCl are added, the sample is filtered with filter paper, the filter paper is digested with con. HCl, and the sample is diluted and analyzed for metals.

Analyte Isolation for Organics Analysis

The determination of organic analytes requires that they be isolated from the sample matrix. Since organic analytes are generally soluble in organic solvents, they can usually be extracted from samples with a suitable solvent. Although extraction works well for nonvolatile and semivolatile analytes, it is not so suitable for volatile organic compounds, which are readily vaporized during sample processing. The volatile materials are commonly isolated by techniques that take advantage of their high vapor pressures.

Solvent Extraction

Method 3500 is a procedure for extracting nonvolatile or semivolatile compounds from a liquid or solid sample. The sample is extracted with an appropriate solvent, dried, and concentrated in a Kuderna-Danish apparatus prior to further processing for analysis.

A number of methods more complicated than Method 3500 have been devised

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for extracting nonvolatile and semivolatile analytes from waste samples. Method 3540 uses extraction with a Soxhlet extractor. This device, illustrated in Chapter 10, Figure 10.6, for the extraction of lipids from biological tissue, provides for recirculation of continuously redistilled fresh solvent over a sample of soils, sludges, and wastes. The sample is first mixed with anhydrous Na_2SO_4 to dry it, then placed inside an extraction thimble in the Soxhlet apparatus, which redistills a relatively small volume of extraction solvent over the sample. After extraction, the sample can be dried, concentrated, and exchanged into another solvent prior to analysis.

Method 3545 uses pressurized fluid extraction at 100˚C and a pressure up to 2000 psi to remove organophilic analyte species from dried solid samples including soils, clays, sediments, sludges, and waste solids. Used for the extraction of semivolatile organic compounds, organophosphorus pesticides, organochlorine pesticides, chlorinated herbicides, and PCBs, it requires less solvent and takes less time than the Soxhlet extraction described above.

Method 3550 uses sonication with ultrasound to expedite the extraction of nonvolatile and semivolatile organic compounds from solids including soils, sludges, and wastes. The procedure calls for subjecting the finely divided dried sample mixed with solvent to ultrasound for a brief period of time. Low-concentration samples can be subjected to multiple extractions with additional fresh solvent.

Although the requirement for specialized high pressure equipment has limited its application, extraction with supercritical carbon dioxide maintained at temperatures and pressures above the critical point where separate liquid and vapor phases do not exist is a very effective means of extracting some organic analytes. Method 3561 is used to extract polycyclic aromatic hydrocarbons such as acenaphthene, benzo(a)pyrene, fluorene, and pyrene from solid samples using a relatively complicated three-step procedure.

Sample Preparation for Volatile Organic Compounds

Several approaches are used to isolate and concentrate volatile analytes from waste samples for subsequent measurement. Some of these based on **headspace analysis** involve evaporation of volatile substances into the space above the sample (headspace) in a closed container. Method 5021, “Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis,” is used to isolate volatile organic compounds, such as benzene, bromomethane, chloroform, 1,4-dichlorobenzene, dichloromethane, styrene, toluene, vinyl chloride, and the xylene isomers, from soil, sediment, or solid waste samples for determination by gas chromatography or gas chromatography/mass spectrometry.

In addition to headspace analysis, purge-and-trap procedures can be employed that drive volatile analytes from a sample and collect them on an adsorbent column for subsequent analysis. Distillation techniques, including azeotropic distillation and vacuum distillation are also used to isolate volatile analytes.

Sample Cleanup

Most waste, soil, and sediment samples result in extraction of extraneous substances that can result in the observation of extraneous peaks, be detrimental to

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peak resolution and column efficiency, and be damaging to expensive columns and detectors. As shown in Table 26.5, **sample cleanup** refers to a number of measures that can be taken to remove these constituents from sample extracts by several procedures. Sample cleanup may involve distillation, partitioning with immiscible solvents, adsorption chromatography, gel permeation chromatography, or the chemical destruction of interfering substances with acid, alkali, or oxidizing agents; two or more of these techniques may be used in combination. The most widely applicable cleanup technique is gel permeation chromatography, which can be used to separate substances with high molecular weights from the analytes of interest. Treatment by adsorption column chromatography with alumina, Florisil, or silica gel can be used to isolate a relatively narrow polarity range of analytes away from interfering substances. Acid-base partitioning can be used in the determination of materials such as chlorophenoxy herbicides and phenols to separate acidic, basic, and neutral organics.

Table 26.5 Sample Cleanup Techniques and Their Applications

Number	Type	Applications
3610	Alumina column	Phthalate esters, nitrosamines
3611	Alumina column cleanup and separation of petroleum wastes	Polycyclic aromatic hydrocarbons, petroleum wastes
3620	Florisil column	Phthalate esters, nitrosamines, organochlorine pesticides, PCBs, chlorinated hydrocarbons, organophosphorus pesticides
3630	Silica gel	Polycyclic aromatic hydrocarbons
3630(b)	Silica gel	Phenols
3640	Gel permeation chromatography	Phenols, phthalate esters, nitrosamines, organochlorine pesticides, PCBs, nitroaromatics, cyclic ketones, polycyclic aromatic hydrocarbons, chlorinated hydrocarbons, organophosphorus pesticides, priority pollutant semivolatiles
3650	Acid-base liquid/liquid partition	Phenols, priority pollutant semivolatiles
3660	Sulfur cleanup	Organochlorine pesticides, PCBs, Priority pollutant semivolatiles

Alumina column cleanup makes use of highly porous granular aluminum oxide. Available in acidic, neutral, and basic pH ranges, this solid is packed into a column topped with a water-absorbing substance over which the sample is eluted with a suitable solvent, which leaves interferences on the column. After elution, the sample is concentrated, exchanged with another solvent if necessary, then analyzed. Florisil

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is an acidic magnesium silicate and a registered trade name of Floridin Co. It is used in a column cleanup procedure in a manner similar to alumina. Silica gel is a weakly acidic amorphous silicon oxide. It can be activated by heating for several hours at 150–160˚C and used for the separation of hydrocarbons. Deactivated silica gel containing 10–20% water acts as an adsorbent for compounds with ionic and nonionic functionalities such as dyes, alkali metal cations, terpenoids, and plasticizers. It is used in a column as described for alumina above. Gel-permeation chromatography separates solutes by size carried over a hydrophobic gel by organic solvents. A gel must be chosen that will separate the appropriate size range of analytes and interferences. The gel is preswelled before loading onto a column and flushed extensively with solvent before the sample is introduced for separation.

26.6 TOXICITY CHARACTERISTIC LEACHING PROCEDURE

The **Toxicity Characteristic Leaching Procedure** (**TCLP**) is specified to determine the potential toxicity hazard of various kinds of wastes.[4] The test was designed to estimate the availability to organisms of both inorganic and organic species in hazardous materials present as liquids, solids, or multiple phase mixtures by producing a leachate, the TCLP extract, which is analyzed for the specific toxicants listed in Table 26.6.

The procedure for conducting the TCLP is rather involved. The procedure need not be run at all if a total analysis of the sample reveals that none of the pollutants specified in the procedure could exceed regulatory levels. At the opposite end of the scale, analysis of any of the liquid fractions of the sample showing that any regulated species would exceed regulatory levels even after the dilutions involved in the TCLP measurement have been carried out designate the sample as hazardous, and the TCLP measurement is not required.

In conducting the TCLP test, if the waste is a liquid containing less than 0.5% solids, it is filtered through a 0.6–0.8 μm glass fiber filter and the filtrate is designated as the TCLP extract. At solids levels exceeding 0.5%, any liquid present is filtered off for separate analysis and the solid is extracted to provide a TCLP extract (after size reduction, if the particles exceed certain size limitations). The choice of the extraction fluid is determined by the pH of the aqueous solution produced from shaking a mixture of 5 g of solids and 96.5 mL of water. If the pH is less than 5.0, a pH 4.93 acetic acid/sodium acetate buffer is used for extraction; otherwise, the extraction fluid used is a pH of 2.88±0.05 solution of dilute acetic acid. Extractions are carried out in a sealed container rotated end-over-end for 18 hours. The liquid portion is then separated and analyzed for the specific substances given in Table 26.6. If values exceed the regulatory limits, the waste is designated as “toxic.”

26.7 ATMOSPHERIC MONITORING

The atmosphere is a particularly difficult analytical system because of the very low levels of substances to be analyzed; sharp variations in pollutant level with time and location; differences in temperature and humidity; and difficulties encountered in reaching desired sampling points, particularly those substantially above the earth’s surface. These conditions make the acquisition of representative atmospheric samples

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Table 26.6 Contaminants Determined in TCLP Procedure

EPA hazardous-waste number	Contaminant	Regulatory level, mg/L
Heavy metals (metalloids)		
D004	Arsenic	5.0
D005	Barium	100.0
D006	Cadmium	1.0
D007	Chromium	5.0
D008	Lead	5.0
D009	Mercury	0.2
D010	Selenium	1.0
D011	Silver	5.0
Organics		
D018	Benzene	0.5
D019	Carbon tetrachloride	0.5
D021	Chlorobenzene	100.0
D022	Chloroform	6.0
D023	*o*-Cresol	200.0[1]
D024	*m*-Cresol	200.0[1]
D025	*p*-Cresol	200.0[1]
D026	Cresol	200.0[1]
D027	1,4-Dichlorobenzene	7.5
D028	1,2-Dichloroethane	0.5
D029	1,1-Dichloroethylene	0.7
D030	2,4-Dinitrotoluene	0.13[2]
D032	Hexachlorobenzene	0.13[2]
D033	Hexachlorobutadiene	0.5
D034	Hexachloroethane	3.0
D035	Methylethyl ketone	200.0
D036	Nitrobenzene	2.0[2]
D037	Pentachlorophenol	100.0
D038	Pyridine	5.0[2]
D039	Tetrachloroethylene	0.7
D040	Trichloroethylene	0.5
D041	2,4,5-Trichlorophenol	400.0
D042	2,4,6-Trichlorophenol	2.0
D043	Vinyl chloride	0.2
Pesticides		
D012	Endrin	0.02
D013	Lindane	0.4
D014	Methoxychlor	10.0
D015	Toxaphene	0.5
D016	2,4-D	10.0
D017	2,4,5-TP (Silvex)	1.0
D020	Chlordane	0.03
D031	Heptachlor (and its epoxide)	0.008

[1] If *o*-, *m*-, and *p*-Cresol concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level of total cresol is 200 mg/L.

[2] Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.

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particularly challenging. The ideal atmospheric analysis techniques are those that work successfully without sampling, such as long-path laser resonance absorption monitoring. For most analyses, however, various types of sampling are required. In some very sophisticated monitoring systems, samples are collected and analyzed automatically and the results are transmitted to a central receiving station. Often, however, a batch sample is collected for later chemical analysis. Figure 26.2 illustrates the effect of duration of sampling upon observed values of air pollutant levels.

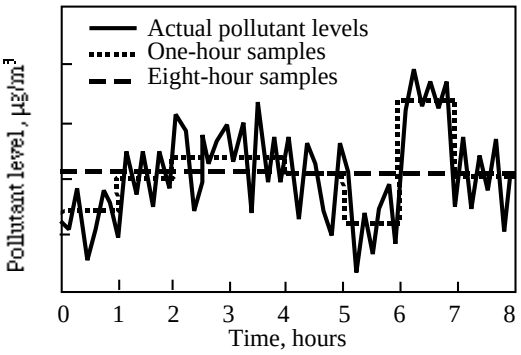


Figure 26.2 Effect of duration of sampling upon observed values of air pollutant levels.

The most straightforward technique for the collection of particles is sedimentation. A sedimentation collector may be as simple as a glass jar equipped with a funnel. Liquid is sometimes added to the collector to prevent the solids from being blown out. Filtration is the most common technique for sampling particulate matter. Filters composed of fritted (porous) glass, porous ceramics, paper fibers, cellulose fibers, fiberglass, asbestos, mineral wool, or plastic can be used. A special type of filter is the membrane filter, which yields high flow rates with small, moderately uniform pores. Impingers, as the name implies, collect particles from a relatively high-velocity air stream directed at a surface.

Sampling for vapors and gases may range from methods designed to collect only one specific pollutant to those designed to collect all pollutants. Essentially all pollutants can be removed from an air sample cryogenically by freezing or by liquifying the air in collectors maintained at a low temperature. Absorption in a solvent, such as by bubbling the gas through a liquid, can be used for the collection of gaseous pollutants. Adsorption, in which a gas collects on the surface of a solid, is particularly useful for the collection of samples to be analyzed by gas chromatography.

Methods of Air Pollutant Analysis

A very large number of different analytical techniques are used for atmospheric pollutant analysis. A summary of some of the main instrumental techniques for air monitoring is presented in Table 26.7.

The U.S. Environmental Protection Agency specifies reference methods of analysis for selected air pollutants to determine compliance with the primary and secondary national ambient air quality standards for those pollutants. These methods are

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published annually in the *Code of Federal Regulations*.[5] These methods are not necessarily state-of-the art, and, in some cases, are outdated and cumbersome. However, they provide proven reliable measurements for regulatory and legal purposes.

Table 26.7 The Main Techniques Used for Air Pollutant Analysis

Pollutant	Method	Potential interferences
SO_2 (total S)	Flame photometric (FPD)	H_2S, CO
SO_2	Gas chromatography (FPD)	H_2S, CO
SO_2	Spectrophotometric (pararosaniline wet chemical)	H_2S, HCl, NH_3, NO_2, O_3
SO_2	Electrochemical	H_2S, HCl, NH_3, NO, NO_2, O_3, C_2H_4,
SO_2	Conductivity	HCl, NH_3, NO_2
SO_2	Gas-phase spectrophotometric	NO, NO_2, O_3,
O_3	Chemiluminescent	H_2S
O_3	Electrochemical	NH_3, NO_2, SO_2
O_3	Spectrophotometric (potassium iodide reaction, wet chemical)	NH_3, NO_2, NO, SO_2
O_3	Gas-phase spectrophotometric	NO_2, NO, SO_2
CO	Infrared	CO_2 (at high levels)
CO	Gas chromatography	- - -
CO	Electrochemical	NO, C_2H_4
CO	Catalytic combustion-thermal detection	NH_3
CO	Infrared fluorescence	- - -
CO	Mercury replacement ultraviolet photometric	C_2H_4
NO_2	Chemiluminescent	NH_3, NO, NO_2, SO_2
NO_2	Spectrophotometric (azo-dye reaction, wet chemical)	NO, SO_2, NO_2, O_3
NO_2	Electrochemical	HCl, NH_3, NO, NO_2, SO_2, O_3, CO
NO_2	Gas-phase spectrophotometric	NH_3, NO, NO_2, SO_2, CO
NO_2	Conductivity	HCl, NH_3, NO, NO_2, SO_2

Determination of Sulfur Dioxide

The reference method for the analysis of sulfur dioxide is the spectrophotometric West-Gaeke pararosaniline method. It uses a collecting solution of 0.04 M potassium tetrachloromercurate to collect sulfur dioxide according to the following reaction:

$$HgCl_4^{2-} + SO_2 + H_2O \rightarrow HgCl_2SO_3^{2-} + 2H^+ + 2Cl^- \quad (26.7.1)$$

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The $HgCl_2SO_3^{2-}$ complex stabilizes readily oxidized sulfur dioxide from reaction with oxidants such as ozone and nitrogen oxides. For analysis, sulfur dioxide in the scrubbing medium is reacted with formaldehyde:

$$HCHO + SO_2 + H_2O \rightarrow HOCH_2SO_3H \qquad (26.7.2)$$

The adduct formed is then reacted with uncolored organic pararosaniline hydrochloride to produce a red-violet dye that is measured spectrophotometrically.

Performed manually, the West-Gaeke method for sulfur dioxide analysis is cumbersome and complicated. However, the method has been refined to the point that it can be done automatically with continuous-monitoring equipment. A block diagram of such an analyzer is shown in Figure 26.3.

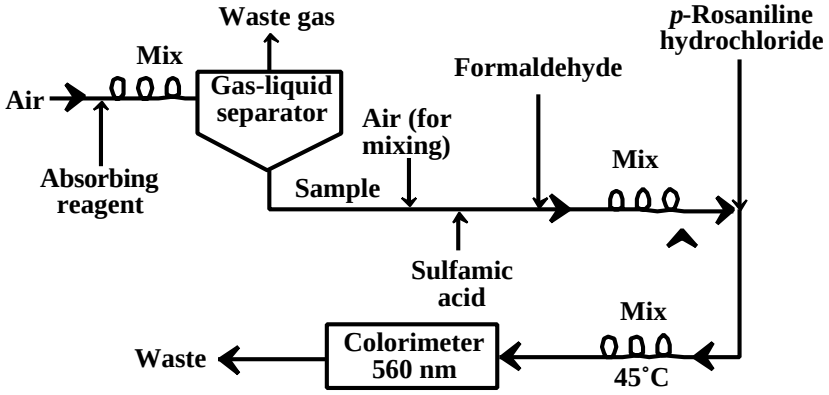


Figure 26.3 Block diagram of an automated system for the determination of sulfur dioxide by the pararosaniline method.

Several types of sulfur dioxide monitors are based on amperometry, in which an electrical current is measured that is proportional to the SO_2 in a collecting solution. Sulfur dioxide can be determined using ion chromatography by bubbling SO_2 through hydrogen peroxide solution to produce SO_4^{2-}, followed by analysis of the sulfate by ion chromatography, a method that separates ions on a chromatography column and detects them very sensitively by conductivity measurement. Flame photometry, sometimes in combination with gas chromatography, is used for the detection of sulfur dioxide and other gaseous sulfur compounds. The gas is burned in a hydrogen flame, and the sulfur emission line at 394 nm is measured.

Several direct spectrophotometric methods are used for sulfur dioxide measurement, including nondispersive infrared absorption, Fourier transform infrared analysis (FTIR), ultraviolet absorption, molecular resonance fluorescence, and second-derivative spectrophotometry. The principles of these methods are the same for any gas measured.

Nitrogen Oxides

Gas-phase chemiluminescence is the favored method of NO_x analysis. The general phenomenon of chemiluminescence was defined in Chapter 14, Section 14.8. It results from the emission of light from electronically excited species formed by a

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chemical reaction. In the case of NO, ozone is used to bring about the reaction, producing electronically excited nitrogen dioxide:

$$NO + O_3 \rightarrow NO_2^* + O_2 \quad (26.7.3)$$

The species loses energy and returns to the ground state through emission of light in the 600–3000 nm range. The emitted light is measured by a photomultiplier; its intensity is proportional to the concentration of NO. A schematic diagram of the device used is shown in Figure 26.4.

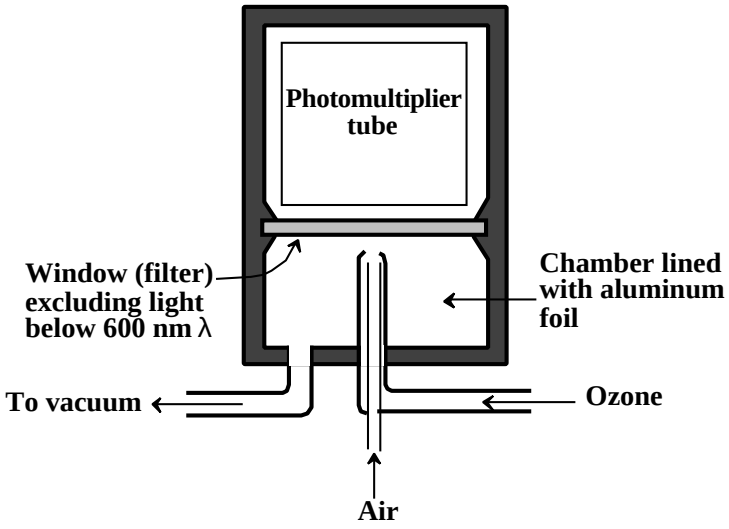


Figure 26.4 Chemiluminescence detector for NO_X.

Since the chemiluminescence detector system depends upon the reaction of O_3 with NO, it is necessary to convert NO_2 to NO in the sample prior to analysis. This is accomplished by passing the air sample over a thermal converter, which brings about the desired conversion. Analysis of such a sample gives NO_X, the sum of NO and NO_2. Chemiluminescence analysis of a sample that has not been passed over the thermal converter gives NO. The difference between these two results is NO_2.

This analysis technique is illustrative of chemiluminescence analysis in general. Chemiluminescence is an inherently desirable technique for the analysis of atmospheric pollutants because it avoids wet chemistry, is basically simple, and lends itself well to continuous monitoring and instrumental methods. Another chemiluminescence method, that employed for the analysis of ozone, is described below.

Analysis of Oxidants

The atmospheric oxidants that are commonly determined include ozone, hydrogen peroxide, organic peroxides, and chlorine. The classic manual method for the analysis of oxidants is based upon their oxidation of I^- ion followed by spectrophotometric measurement of the product. The sample is collected in 1% KI buffered at pH 6.8. Oxidants react with I^- ion as shown by the following reaction of ozone:

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$$O_3 + 2H^+ + 3I^- \rightarrow I_3^- + O_2 + H_2O \quad (26.7.4)$$

The absorbance of the colored I_3^- product is measured spectrophotometrically at 352 nm. Generally, the level of oxidant is expressed in terms of ozone, although it should be noted that not all oxidants—PAN, for example—react with the same efficiency as O_3. Oxidation of I^- as shown in the above reaction can be used to determine oxidants in a concentration range of several hundredths of a part per million to approximately 10 ppm. Nitrogen dioxide gives a limited response to the method, and reducing substances interfere seriously.

The currently favored method for oxidant analysis uses the chemiluminescent reaction between ozone and ethylene. This reaction emits light at a maximum intensity at 435 nm. The intensity of emitted light is directly proportional to the level of ozone.

Analysis of Carbon Monoxide

Carbon monoxide is analyzed in the atmosphere by nondispersive infrared spectrometry. This technique depends upon the fact that carbon monoxide absorbs infrared radiation strongly at certain wavelengths. Therefore, when such radiation is passed through a long (typically 100 cm) cell containing trace levels of carbon monoxide, more of the infrared radiant energy is absorbed.

A nondispersive infrared spectrometer differs from standard infrared spectrometers in that the infrared radiation from the source is not dispersed according to wavelength by a prism or grating. The nondispersive infrared spectrometer is made very specific for a given compound, or type of compound, by using the sought-for material as part of the detector, or by placing it in a filter cell in the optical path. A diagram of a nondispersive infrared spectrometer selective for CO is shown in Figure 26.5. Radiation from an infrared source is “chopped” by a rotating device so that it alternately passes through a sample cell and a reference cell. In this particular instrument, both beams of light fall on a detector filled with CO gas and separated into two compartments by a flexible diaphragm. The relative amounts of infrared radiation absorbed by the CO in the two sections of the detector depend upon the level of CO in the sample. The difference in the amount of infrared radiation absorbed in the two compartments causes slight differences in heating, so that the diaphragm bulges slightly toward one side. Very slight movement of the diaphragm can be detected and recorded. By means of this device, carbon monoxide can be measured from 0–150 ppm, with a relative accuracy of ±5% in the optimum concentration range.

Flame-ionization gas chromatography detection can also be used for the analysis of carbon monoxide. This detector system is selective for hydrocarbons, and conversion of CO to methane in the sample is required. This is accomplished by reaction with hydrogen over a nickel catalyst at 360 ˚C:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (26.7.5)$$

A major advantage of this approach is that the same basic instrumentation can be used to measure hydrocarbons.

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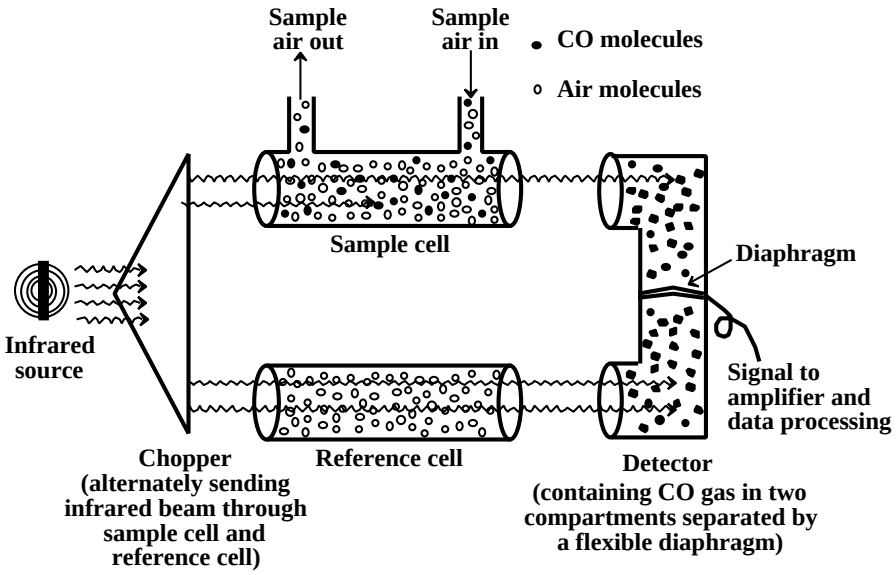


Figure 26.5 Nondispersive infrared spectrometer for the determination of carbon monoxide in the atmosphere.

Determination of Hydrocarbons and Organics

Monitoring of hydrocarbons in atmospheric samples takes advantage of the very high sensitivity of the hydrogen flame ionization detector to measure this class of compounds. Known quantities of air are run through the flame ionization detector 4 to 12 times per hour to provide a measure of total hydrocarbon content.

In some cases, it is important to have a method to determine individual organics because of their toxicities, ability to form photochemical smog, as indicators of photochemical smog, and as a means of tracing sources of pollution. Numerous techniques have been published for the determination of organic compounds in the atmosphere. For example, whole-air samples can be collected in Tedlar bags, and the organic analytes concentrated cryogenically at -180˚C, then thermally desorbed and measured with high-resolution capillary column gas chromatography.

Analysis of Particulate Matter

Particles are almost always removed from air or gas (such as exhaust flue gas) prior to analysis. The two main approaches to particle isolation are filtration and removal by methods that cause the gas stream to undergo a sharp bend such that particles are collected on a surface.

The method commonly used for determining the quantity of total suspended particulate matter in the atmosphere draws air over filters that remove the particles. This device, called a **Hi-Vol sampler** (Figure 26.6), is essentially a glorified vacuum cleaner that draws air through a filter. The samplers are usually placed under a shelter that excludes precipitation and particles larger than about 0.1 mm in

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diameter, favoring collection of particles up to 25–50 μm diameter. These devices efficiently collect particles from a large volume of air, typically 2000 m^3, and typically over a 24-hour period.

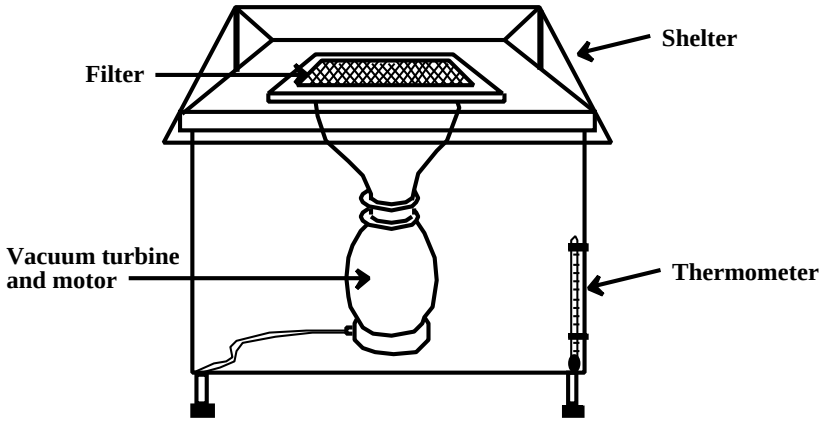


Figure 26.6 Hi-Vol sampler for the collection of particulate matter from the atmosphere for analysis.

The filters used in a Hi-Vol sampler are usually composed of glass fibers and have a collection efficiency that is at least 99% for particles with 0.3 μm diameter. Particles with diameters exceeding 100 μm remain on the filter surface, whereas particles with diameters down to approximately 0.1 μm are collected on the glass fibers in the filters. Efficient collection is achieved by using very small-diameter fibers (less than 1 μm) for the filter material.

The technique described here is most useful for determining total levels of particulate matter. Prior to taking the sample, the filter is maintained at 15-35˚C at 50% relative humidity for 24 hours, then weighed. After sampling for 24 hours, the filter is removed and equilibrated for 24 hours under the same conditions used prior to its installation on the sampler. The filter is then weighed and the quantity of particulate matter per unit volume of air is calculated.

Size separation of particles can be achieved by filtration through successively smaller filters in a **stacked filter unit**. Another approach uses the **virtual impactor**, a combination of an air filter and an impactor (discussed below). In the virtual impactor, the gas stream being sampled is forced to make a sharp bend. Particles larger than about 2.5 μm do not make the bend and are collected on a filter. The remaining gas stream is then filtered to remove smaller particles.

Impactors cause a relatively high velocity gas stream to undergo a sharp bend such that particles are collected on a surface impacted by the stream. The device may be called a dry or wet impactor, depending upon whether collecting surface is dry or wet; wet surfaces aid particle retention. Size segregation can be achieved with an impactor because larger particles are preferentially impacted, and smaller particles continue in the gas stream.

A number of chemical analysis techniques can be used to characterize atmospheric pollutants. These include atomic absorption, inductively coupled plasma techniques, X-ray fluorescence, neutron activation analysis, and ion-selective elec-

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trodes for fluoride analysis. Chemical microscopy is an extremely useful technique for the characterization of atmospheric particles. Either visible or electron microscopy can be employed. Particle morphology and shape tell the experienced microscopist a great deal about the material being examined. Reflection, refraction, microchemical tests, and other techniques can be employed to further characterize the materials being examined. Microscopy can be used for determining levels of specific kinds of particles and for determining particle size.

Direct Spectrophotometric Analysis of Gaseous Air Pollutants

From the foregoing discussion, it is obvious that measurement techniques that depend upon the use of chemical reagents, particularly liquids, are cumbersome and complicated. It is a tribute to the ingenuity of instrument designers that such techniques are being applied successfully to atmospheric pollutant monitoring. Direct spectrophotometric techniques are much more desirable when they are available and when they are capable of accurate analysis at the low levels required. One such technique, nondispersive infrared spectrophotometry, was described above for the analysis of carbon monoxide. Three other direct spectrophotometric methods are Fourier transform infrared spectroscopy, tunable diode laser spectroscopy, and, the most important of all, differential optical absorption spectroscopy. These techniques can be used for point air monitoring, in which a sample is monitored at a given point, generally by measurement in a long absorption cell. In-stack monitoring can be performed to measure effluents. A final possibility is the collection of long-line data (sometimes using sunlight as a radiation source), yielding concentrations in units of concentration-length (ppm-meters). If the path length is known, the concentration can be calculated. This approach is particularly useful for measuring concentrations in stack plumes.

The low levels of typical air constituents require long path lengths, sometimes up to several kilometers, for spectroscopic measurements. These can be achieved by locating the radiation source some distance from the detector, by the use of a distant retroreflector to reflect the radiation back to the vicinity of the source, or by cells in which a beam is reflected multiple times to achieve a long path length.

A typical open-path Fourier transform infrared system for remote monitoring of air pollutants uses a single unit (telescope) that functions as both a transmitter and receiver of infrared radiation (Figure 26.7). The radiation is generated by a silicon

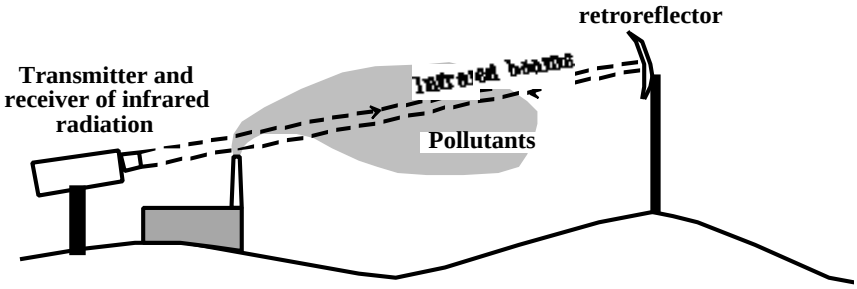


Figure 26.7 FTIR system for remote sensing of air pollutants.

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carbide glower, modulated by a Michaelson inteferometer, and transmitted to a retroreflector, which reflects it back to the telescope, where its intensity is measured. The modulated infrared signal, called an inteferogram, is processed by a mathematical algorithm, the Fourier transform, to give a spectrum of the absorbing substances. This spectrum is fitted mathematically to spectra of the absorbing species to give their concentrations.

Dispersive absorption spectrometers are basically standard spectrometers with a monochromator for selection of the wavelength to be measured. They are used to measure air pollutants by determining absorption at a specified part of the spectrum of the sought-for material. Of course, other gases or particulate matter that absorb or scatter light at the chosen wavelength interfere. These instruments are generally applied to in-stack monitoring. Sensitivity is increased by using long path lengths or by pressurizing the cell.

Second-derivative spectroscopy is a useful technique for trace gas analysis. Basically, this technique varies the wavelength by a small value around a specified nominal wavelength. The second derivative of light intensity versus wavelength is obtained. In conventional absorption spectrophotometry, a decrease in light intensity as the light passes through a sample indicates the presence of at least one substance—and possibly many—absorbing at that wavelength. Second-derivative spectroscopy, however, provides information regarding the change in intensity with wavelength, thereby indicating the presence of specific absorption lines or bands that can be superimposed on a relatively high background of absorption. Much higher specificity is obtained. The spectra obtained by second-derivative spectrometry in the ultraviolet region show a great deal of structure and are quite characteristic of the compounds being observed.

Lidar, which stands for *li*ght *d*etection *a*nd *r*anging (analogous to radar, *ra*dio *d*etection *a*nd *r*anging), is finding numerous applications in atmospheric monitoring. Lidar systems send short pulses of light or infrared radiation into the atmosphere and collect radiation scattered back from molecules or particles in the atmosphere. Computer analysis of the signal enables analysis of species in the atmosphere.

26.8 ANALYSIS OF BIOLOGICAL MATERIALS AND XENOBIOTICS

As defined in Chapter 23, a xenobiotic species is one that is foreign to living systems. The determination of xenobiotic substances in biological materials is very important. The greatest concern with such substances is their presence in human tissues and other samples of human origin. They may also be determined in plant or microbiological samples. The measurement of xenobiotic substances and their metabolites in blood, urine, breath, and other samples of biological origin to determine exposure to toxic substances is called **biological monitoring**. For more detailed current information regarding this area, the reader is referred to excellent reviews of the topic,[6,7] and several books on biological monitoring such as those by Angerer, Draper, Baselt, and Kneip and coauthors, which are listed in the back of this chapter under “Supplementary References,” are available as well.

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Indicators of Exposure to Xenobiotics

Both the type of sample and type of analyte are influenced by what happens to a xenobiotic material when it gets into the body. For some exposures, the entry site composes the sample. This is the case, for example, in exposure to asbestos fibers in the air, which is manifested by lesions to the lung. More commonly, the analyte may appear at some distance from the site of exposure, such as lead in bone that was originally taken in by the respiratory route. In other cases, the original xenobiotic is not even present in the analyte. An example of this is methemoglobin in blood, the result of exposure to aniline absorbed through the skin.

The two major kinds of samples analyzed for xenobiotics exposure are blood and urine. Both of these kinds of samples are analyzed for systemic xenobiotics, which are those that are transported in the body and metabolized in various tissues. Blood is of unique importance as a sample for biological monitoring.

Phase 1 and Phase 2 reaction products of xenobiotics (Chapter 23) tend to be converted to more polar and water soluble metabolites. These are eliminated with the urine, making it a good sample to analyze as evidence of exposure to xenobiotic substances. Urine has the advantage of being a simpler matrix than blood and one that subjects more readily give for analysis. Other kinds of samples that can be analyzed include breath (for volatile xenobiotics and volatile metabolites), air or nails (for trace elements, such as selenium), adipose tissue (fat), and milk (obviously limited to lactating females). Various kinds of organ tissue can be analyzed in cadavers to determine the toxic agent that has caused death by poisoning.

The choice of the analyte actually measured varies with the xenobiotic substance to which the subject has been exposed. Therefore, it is convenient to divide xenobiotic analysis on the basis of the type of chemical species determined. The most straightforward analyte is, of course, the xenobiotic itself. This applies to elemental xenobiotics, especially metals, which are almost always determined in the elemental form. In a few cases, organic xenobiotics can also be determined as the parent compound. However, organic xenobiotics are commonly determined as Phase 1 and Phase 2 reaction products. Often the Phase 1 reaction product is measured, frequently after it is hydrolyzed from the Phase 2 conjugate, using enzymes or acid hydrolysis procedures. Thus, for example, *trans*,*trans*-muconic acid can be measured as evidence of exposure to the parent compound benzene. In other cases, a Phase 2 reaction product is measured, for example, hippuric acid determined as evidence of exposure to toluene. Some xenobiotics or their metabolites form adducts with endogenous materials in the body, which are then measured as evidence of exposure. A simple example is the adduct formed between carbon monoxide and hemoglobin, carboxyhemoglobin. More-complicated examples are the adducts formed by the carcinogenic Phase 1 reaction products of polycyclic aromatic hydrocarbons with DNA or hemoglobin. Another class of analytes consists of endogenous substances produced upon exposure to a xenobiotic material. Methemoglobin formed as a result of exposure to nitrobenzene, aniline, and related compounds is an example of such a substance that does not contain any of the original xenobiotic material. Another class of substance causes measurable alterations in enzyme activity. The most common example of this is the inhibition of acetylcholinesterase enzyme by organophosphates or carbamate insecticides.

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Analysis of Metals in Biological Samples

Several biologically important metals can be determined directly in body fluids, especially urine, by atomic absorption. In the simplest cases, the urine is diluted with water or with acid and a portion analyzed directly by graphite furnace atomic absorption, taking advantage of the very high sensitivity of that technique for some metals. Metals that can be determined directly in urine by this approach include chromium, copper, lead, lithium, and zinc.

Many metals, including cadmium, chromium, copper, lead, manganese, and zinc, are readily determined by atomic absorption or emission in blood or urine samples wet-ashed by heating the sample with strong acid and oxidant to dryness and redissolving the residue in acid. A typical procedure is digestion of blood or urine for cadmium analysis, which consists of mixing the sample with a comparable volume of concentrated nitric acid, heating to a reduced volume, adding 30% hydrogen peroxide oxidant, heating to dryness, and dissolving in nitric acid prior to measurement by atomic absorption or emission. Mixtures of nitric, sulfuric, and perchloric acid are effective for digestion, though somewhat hazardous.

A number of procedures for the determination of metals and biological samples call for the extraction of the metal with an organic chelating agent in order to remove interferences and concentrate the metal to enable detection of low levels. The urine or blood sample can be first subjected to wet ashing to enable extraction of the metal. The availability of strongly chelating extracts for a number of metals has led to the development of procedures in which the metal is extracted from minimally treated blood or urine, then quantified by atomic absorption analysis. The metals for which such extractions can be used include cobalt, lead, and thallium extracted into organic solvent as the dithiocarbamate chelate, and nickel extracted into methylisobutyl ketone as a chelate formed with ammonium pyrrolidinedithiocarbamate.

Methods for several metals or metalloids involve conversion to a volatile form. Arsenic, antimony, and selenium can be reduced to their volatile hydrides, AsH_3, SbH_3, and H_2Se, repectively, which can be determined by atomic absorption or other means. Mercury is reduced to volatile mercury metal, which is evolved from solution and measured by cold vapor atomic absorption.

Determination of Nonmetals and Inorganic Compounds

Relatively few nonmetals require determination in biological samples. One important example is potentially toxic fluoride, which occurs in biological fluids as the fluoride ion, F^-. Fluoride in appropriately processed samples is readily determined potentiometrically with a fluoride ion-selective electrode.

Toxic cyanide can be isolated in a special device called a Conway microdiffusion cell by treatment with acid, followed by collection of the weakly acidic HCN gas that is evolved in a base solution. The cyanide released can be measured spectrophotometrically by formation of a colored species.

Carbon monoxide is readily determined in blood by virtue of the colored carboxyhemoglogin that it forms with hemoglobin using solution absorption spectrophotometry. The procedure consists of measuring the absorbances at wavelengths of 414, 421, and 428 nm of the blood sample, a sample through which

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oxygen has been bubbled to change all the hemoglobin to the oxyhemoglobin form, and a sample through which carbon monoxide has been bubbled to change all the hemoglobin to carboxyhemoglobin. With the appropriate calculations, a percentage conversion to carboxyhemoglobin can be obtained.

Determination of Parent Organic Compounds

A number of organic compounds can be measured as the unmetabolized compound in blood, urine, and breath. In some cases, the sample can be injected along with its water content directly into a gas chromatograph. Direct injection is used for the measurement of acetone, *n*-butanol, dimethylformamide, cyclopropane, halothane, methoxyflurane, diethyl ether, isopropanol, methanol, methyl*n*-butyl ketone, methyl chloride, methylethyl ketone, toluene, trichloroethane, and trichloroethylene.

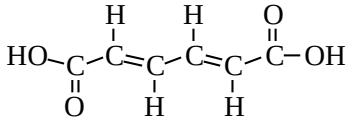
For the determination of volatile compounds in blood or urine, a straightforward approach is to liberate the analyte at an elevated temperature allowing the volatile compound to accumulate in headspace above the sample followed by direct injection of headspace gas into a gas chromatograph. A reagent such as perchloric acid, may be added to deproteinize the blood or urine sample and facilitate release of the volatile xenobiotic compound. Among the compounds determined by this approach are acetaldehyde, dichloromethane, chloroform, carbon tetrachloride, benzene, trichloroethylene, toluene, cyclohexane, and ethylene oxide. Purge-and-trap techniques that evolve volatile analytes from blood or urine in a gas stream and onto a trap for subsequent chromatographic analysis have been developed. Such a technique employing gas chromatographic separation and Fourier transform infrared detection has been described for a number of volatile organic compounds in blood.[8]

Measurement of Phase 1 and Phase 2 Reaction Products

Phase 1 Reaction Products

For a number of organic compounds, the most accurate indication of exposure is to be obtained by determining their Phase 1 reaction products. In cases where a significant fraction of the xenobiotic compound has undergone a Phase 2 reaction, the Phase 1 product can be regenerated by acid hydrolysis.

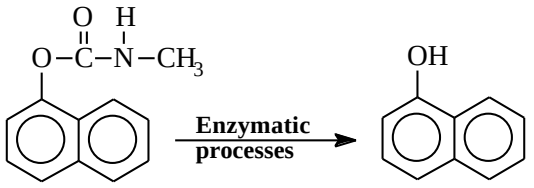
One of the compounds commonly determined as its Phase 1 metabolite is benzene, which is metabolized to phenol in the body (see Chapter 23, Section 23.13 and Figure 23.16). The phenol metabolic product of benzene is measured in urine, usually by gas chromatography. The urine sample is treated with perchloric acid to hydrolyze phenol conjugates and the phenol is extracted into diisopropyl ether for chromatographic analysis. Two other metabolic products of benzene, *trans*,*trans*-muconic acid and S-phenyl mercapturic acid, are now commonly measured as more-specific biomarkers of benzene exposure.



***Trans* , *trans* -muconic acid**

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Insecticidal carbaryl undergoes the following metabolic reaction:



(26.8.1)

Therefore, the determination of 1-naphthol in urine indicates exposure to carbaryl. The 1-naphthol that is conjugated by a Phase 2 reaction is liberated by acid hydrolysis, then determined spectrophotometrically or by chromatography

In addition to the examples discussed above, a number of other xenobiotics are measured by their Phase 1 reaction products. These compounds and their metabolites are listed in Table 26.8. These methods are for metabolites in urine. Normally, the urine sample is acidified to release the Phase 1 metabolites from Phase 2 conjugates that they might have formed and, except where direct sample injection is employed, the analyte is collected as vapor or extracted into an organic solvent. In some cases, the analyte is reacted with a reagent that produces a volatile derivative that is readily separated and detected by gas chromatography.

Phase 2 Reaction Products

Hippuric acids, which are formed as Phase 2 metabolic products from toluene, the xylenes, benzoic acid, ethylbenzene, and closely related compounds, can be determined as biological markers of exposure. The formation of hippuric acid from toluene is shown in Chapter 23, Figure 23.17. Structurally similar 4-methylhippuric acid is produced metabolically from *p*-xylene by the same process that produces hippuric acid from toluene. Other metabolites that may be formed from aryl solvent precursors include mandelic acid and phenylgloxylic acid.

Exposure to toluene can be detected by extracting hippuric acid from acidified urine into diethyl ether/isopropanol and direct ultraviolet absorbance measurement of the extracted acid at 230 nm. When the analysis is designed to detect the xylenes, ethylbenzene, and related compounds, several metabolites related to hippuric acid may be formed and the ultraviolet spectrometric method does not give the required specificity. However, the various acids produced from these compounds can be extracted from acidified urine into ethyl acetate, derivatized to produce volatile species, and quantified by gas chromatography.

A disadvantage to measuring toluene exposure by hippuric acid is the production of this metabolite from natural sources, and the determination of tolulylmercapturic acid is now favored as a biomarker of toluene exposure.[9] An interesting sidelight is that dietary habits can cause uncertainties in the measurement of xenobiotic metabolites. An example of this is the measurement of workers' exposure to 3-chloropropene by the production of allylmercapturic acid.[10] This metabolite is also produced by garlic, and garlic consumption by workers was found to be a confounding factor in the method. Thiocyanate monitored as evidence of exposure to cyanide is increased markedly by the consumption of cooked cassava!

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Table 26.8 Phase 1 Reaction Products of Xenobiotics Determined

Parent compound	Metabolite	Method of analysis
Cyclohexane	Cyclohexanol	Extraction of acidified, hydrolyzed urine with dichloromethane followed by gas chromatography
Diazinone	Organic phosphates	Colorimetric determination of phosphates
p-Dichlorobenzene	2,5-Dichlorophenol	Extraction into benzene, gas chromatographic analysis
Dimethylformamide	Methylformamide	Gas chromatography with direct sample introduction
Dioxane	β-hydroxyethoxyacetic acid	Formation of volatile methyl ester, gas chromatography
Ethybenzene	Mandelic acid and related aryl acids	Extraction of acids, formation of volatile derivatives, gas chromatography
Ethylene glycol monomethyl ether	Methoxyacetic acid	Extracted with dichloromethane, converted to volatile methyl derivative, gas chromatography
Formaldehyde	Formic acid	Gas chromatography of volatile formic acid deriviative
Hexane	2,5-Hexanedione	Gas chromatography after extraction with dichloromethane
n-Heptane	2-Heptanone, valerolactone, 2,5-heptanedione	Measurement in urine by GC/MS
Isopropanol	Acetone	Gas chromatography following extraction with methylethyl ketone
Malathion	Organic phosphates	Colorimetric determination of phosphates
Methanol	Formic acid	Gas chromatography of volatile formic acid derivative
Methyl bromide	Bromide ion	Formation of volatile organobromine compounds, gas chromatography
Nitrobenzene	*p*-Nitrophenol	Gas chromatography of volatile derivative
Parathion	*p*-Nitrophenol	Gas chromatography of volatile derivative
Polycyclic aryl hydrocarbons	1-Hydroxypyrene	HPLC of urine

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Table 26.8. (Cont.)

Styrene	Mandelic acid	Extraction of acids, formation of volatile derivatives, gas chromatography
Tetrachloroethylene, trichloroethane, trichloroethylene	Trichloroacetic acid	Extracted into pyridine and measured colorimetrically

Mercapturates

Mercapturates are proving to be very useful Phase 2 reaction products for measuring exposure to xenobiotics, especially because of the sensitive determination of these substances by HPLC separation, and fluorescence detection of their *o*-phthaldialdehyde derivatives. In addition to toluene mentioned above, the xenobiotics for which mercapturates can be monitored include styrene, structurally similar to toluene; acrylonitrile; allyl chloride; atrazine; butadiene; and epichlorohydrin.

The formation of mercapturates or mercapturic acid derivatives by metabolism of xenobiotics is the result of a Phase 2 conjugation by glutathione. **Glutathione** (commonly abbreviated GSH) is a crucial conjugating agent in the body. This compound is a tripeptide, meaning that it is composed of three amino acids linked together. These amino acids and their abbreviations are glutamic acid (Glu), cysteine (Cys), and glycine (Gly). The formula of glutathione can be represented as illustrated in Figure 26.8, where the SH is shown specifically because of its crucial role

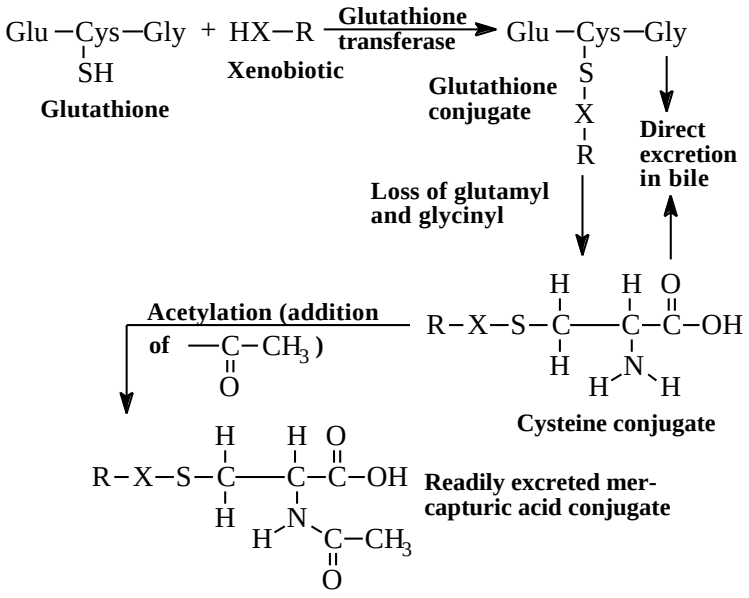


Figure 26.8 Glutathione conjugate of a xenobiotic species (HX-R) followed by formation of glutathione and cysteine conjugate intermediates (which may be excreted in bile) and acetylation to form readily excreted mercapturic acid conjugate.

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in forming the covalent link to a xenobiotic compound. Rarely, glutathione conjugate may be excreted directly, but it usually undergoes further biochemical reactions that produce mercapturic acids (compounds with N-acetylcysteine attached) or other species. The specific mercapturic acids can be monitored as biological markers of exposure to the xenobiotic species that result in their formation. The overall process for the production of mercapturic acids as applied to a generic xenobiotic species, HX-R (see previous discussion), is illustrated in Figure 26.8.

Determination of Adducts

Determination of adducts is often a useful and elegant means of measuring exposure to xenobiotics. Adducts, as the name implies, are substances produced when xenobiotic substances add to endogenous chemical species. The measurement of carbon monoxide from its hemoglobin adduct was discussed in above. In general, adducts are produced when a relatively simple xenobiotic molecule adds to a large macromolecular biomolecule that is naturally present in the body. The fact that adduct formation is a mode of toxic action, such as occurs in the methylation of DNA during carcinogenesis (Chapter 22, Section 23.8), makes adduct measurement as a means of biological monitoring even more pertinent.

Adducts to hemoglobin are perhaps the most useful means of biological monitoring by adduct formation. Hemoglobin is, of course, present in blood, which is the most accurate type of sample for biological monitoring. The measurement of hemoglobin adducts is emerging as a method of choice for a number of xenobiotics including acrylamide, acrylonitrile, 1,3-butadiene, 3,3'-dichlorobenzidine, ethylene oxide, and hexahydrophthalic anhydride.

Immunological Methods of Xenobiotics Analysis

As discussed in Chapter 25, Section 25.12, immunoassay methods offer distinct advantages in specificity, selectivity, simplicity, and costs. Although used in simple test kits for blood-glucose and pregnancy testing, immunoassay methods have been limited in biological monitoring of xenobiotics, in part because of interferences in complex biological systems. Because of their inherent advantages, however, it can be anticipated that immunoassays will grow in importance for biological monitoring of xenobiotics.

CHAPTER SUMMARY

The chapter summary below is presented in a programmed format to review the main points covered in this chapter. It is used most effectively by filling in the blanks, referring back to the chapter as necessary. The correct answers are given at the end of the summary.

The commonly determined physical properties of water are [1]_____ _____.
Usually, [2]_____ samples must be collected for chemical and biological analysis because [3]_____

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_____. A composite sample has the advantage of providing [4]_____. A conventional solid phase extractor collects analyte on [5]_____ _____. The most general method of sample preservation is [6]_____ _____. Water samples that can be kept longest before analysis are those to be analyzed for [7]_____. Acidity, alkalinity, and hardness in water can all be determined by [8]_____. Arsenic, boron, nitrate, and surfactants in water can all be analyzed by [9]_____. EPA methods 601, 608, 613, and 1624 are all methods that use [10]_____ _____ to determine [11]_____ in water. A technique that uses a dissolved oxidizing agent promoted by ultraviolet light is used to measure [12]_____ in water. Metals in water are normally determined by some form of [13]_____ analysis. The methods included in the "SW-846" compilation are for the analysis of [14]_____. To analyze a solid-waste sample by atomic spectrophotmetric techniques for metals, it must first be [15]_____. In analyzing solid-waste samples, microwave heating can be used to [16]_____ _____. Means of isolating nonvolatile and semivolatile analytes from solid waste samples include [17]_____ _____ _____.Two major approaches used to isolate and concentrate volatile analytes from waste samples for subsequent measurement are [18]_____ _____. Sample cleanup refers to processes used to [19]_____ _____. Materials used for this purpose include [20]_____ _____. The [21]_____ _____ is designed to estimate the availability to organisms of both inorganic and organic species in hazardous materials. The extractants used in this procedure are [22]_____. The atmosphere is a particularly difficult analytical system because of [23]_____ _____ _____ _____. The ideal atmospheric analysis techniques are those that [24]_____ _____. The most common technique for sampling atmospheric particulate matter is [25]_____. The reference method for the analysis of sulfur dioxide is the [26]_____ _____ method. A method for the determination of gaseous inorganic air pollutants that involves their conversion to ions is [27]_____. The favored method of NO_x analysis is [28]_____, for which the reaction producing a measurable signal is [29]_____ _____. The atmospheric oxidants that are commonly determined include [30]_____, the classic manual method for which involves [31]_____. The currently favored method for oxidant (ozone) analysis uses [32]_____ _____. Carbon monoxide is commonly analyzed in the atmosphere by [33]_____.

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Monitoring hydrocarbons in atmospheric samples uses [34]_____ _____. The device commonly used to sample atmospheric particles is the [35]_____, which can sample 2000 m^3 over a 24-hour period. Impactors used to sample atmospheric particles cause a relatively high velocity gas stream to [36]_____, such that particles are collected on a surface. Direct spectrophotometric techniques for the measurement of air pollutants include, in addition to nondispersive infrared spectrophotometry, [37]_____ _____. Lidar systems for atmospheric pollutant measurement operate by [38]_____ _____ _____. Biological monitoring is [39]_____ _____ _____. The two major kinds of samples analyzed for xenobiotics exposure are [40]._____. The most straightforward analyte to measure in xenobiotics analysis is [41]_____ _____, and other analytes that actually include the xenobiotic material or its metabolites are [42]_____ _____. Metals in biological samples are most commonly determined by [43]_____ _____. Nonmetals commonly determined in biological samples include [44]_____. Two metabolic products other than phenol that can be measured as evidence of exposure to benzene are [45]_____. Exposure to toluene, the xylenes, benzoic acid, and ethylbenzene can be determined by measuring [46]_____. A class of metabolites useful for measuring exposure to xenobiotic materials and that are formed by a process beginning with conjugation by glutathion are [47]_____. A limitation to using immunoassay methods for xenobiotics analysis is [48]_____ _____.

Answers to Chapter Summary

1. color, residue (solids), odor, temperature, specific conductance, and turbidity
2. separate
3. the sampling and preservation techniques differ significantly
4. an overall picture from only one analysis
5. an extracting solid in a column
6. refrigeration to 4°C
7. metals
8. titration
9. solution spectrophotometry
10. gas chromatography
11. organics
12. total organic carbon
13. atomic spectrophotometric

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14. solid wastes
15. digested to get the analyte metals in solution
16. assist digesting the samples
17. Soxhlet extraction, pressurized fluid extraction, sonication with ultrasound and supercritical fluid extraction
18. headspace analysis and purge-and-trap
19. remove extraneous interfering matter from samples
20. alumina, silica gel, and Florisil
21. Toxicity Characteristic Leaching Procedure
22. acetic acid/sodium acetate buffer
23. the very low levels of substances to be analyzed; sharp variations in pollutant level with time and location; differences in temperature and humidity; and difficulties encountered in reaching desired sampling points
24. work successfully without sampling
25. filtration
26. spectrophotometric West-Gaeke pararosaniline
27. ion chromatography
28. gas-phase chemiluminescence
29. $NO + O_3 \rightarrow NO_2^* + O_2$
30. ozone, hydrogen peroxide, organic peroxides, and chlorine
31. oxidation of I^- to I_3^-
32. the chemiluminescent reaction between ozone and ethylene
33. nondispersive infrared spectrometry
34. the hydrogen flame ionization detector
35. Hi-Vol sampler
36. undergo a sharp bend
37. Fourier transform infrared spectroscopy, tunable diode laser spectroscopy, and differential optical absorption spectroscopy
38. sending short pulses of light or infrared radiation into the atmosphere and collecting radiation scattered back from molecules or particles in the atmosphere
39. the measurement of xenobiotic substances and their metabolites in blood, urine, breath, and other samples of biological origin
40. blood and urine
41. the xenobiotic itself
42. Phase 1 and Phase 2 reaction products and adducts with endogenous substances
43. atomic spectrometric
44. fluoride, carbon monoxide, and cyanide
45. *trans*,*trans*-muconic acid and S-phenyl mercapturic acid
46. hippuric acid compounds
47. mercapturates
48. interferences in complex biological systems

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QUESTIONS AND PROBLEMS

1. A soluble water pollutant forms ions in solution and absorbs light at 535 nm. What are two physical properties of water influenced by the presence of this pollutant?

2. A sample was taken from the bottom of a deep, stagnant lake. Upon standing, bubbles were evolved from the sample; the pH went up; and a white precipitate formed. From these observations, what can be said about the dissolved CO_2 and hardness in the water?

3. For which of the following analytes can nitric acid be used as a water sample preservative: H_2S; CO_2; metals; coliform bacteria; cyanide?

4. In the form of what compound is oxygen fixed in the Winkler analysis of O_2?

5. Manganese from a standard solution was oxidized to MnO_4^- and diluted such that the final solution contained 1.00 mg/L of Mn. This solution had an absorbance of 0.316. A 10.00 mL wastewater sample was treated to develop the MnO_4 color and diluted to 250.0 mL. The diluted sample had an absorbance of 0.296. What was the concentration of Mn in the original wastewater sample?

6. A water sample was run through the colorimetric procedure for the analysis of nitrate, giving 55.0% transmittance. A sample containing 1.00 ppm nitrate run through the exactly identical procedure gave 24.6% transmittance. What was the concentration of nitrate in the first sample?

7. What is the molar concentration of HCl in a water sample containing HCl as the only contaminant and having a pH of 3.80?

8. A 200-mL sample of water required 25.12 mL of 0.0200N standard H_2SO_4 for titration to the methyl orange endpoint, pH 4.5. What was the total alkalinity of the original sample?

9. Analysis of a lead-containing sample by graphite-furnace atomic absorption analysis gave a peak of 0.075 absorbance units when 50 microliters of pure sample was injected. Lead was added to the sample such that the added concen-

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tration of lead was 6.0 micrograms per liter. Injection of 50 microliters of "spiked" sample gave an absorbance of 0.115 absorbance units. What was the concentration of lead in the original sample?

10. In a 2.63×10^{-4} M standard fluoride solution, a fluoride electrode read -0.100 volts versus a reference electrode, and it read -0.118 volts in an appropriately processed fluoride sample. Considering Equation 25.8.3 in Chapter 25, what was the concentration of fluoride in the sample?
11. Why is magnesium-EDTA chelate added to a magnesium-free water sample before it is to be titrated with EDTA for Ca^{2+} ?
12. For what type of sample is the flame-ionization detector most useful?
13. Explain the uses of microwave in hazardous waste analysis. How is ultrasound employed in hazardous waste analysis?
14. Does sample digestion necessarily give an analysis leading to total metals? Why might it not be advantageous to measure total metals in a sample?
15. What is the distinction between a Kuderna-Danish apparatus and a Soxhlet apparatus?
16. How is anhydrous Na_2SO_4 used in organics analysis?
17. What is the purpose of sample cleanup? Why is cleanup more commonly applied to samples to be analyzed for organic contaminants than for metals?
18. What is the principle of immunoassay? What makes it specific for compounds or narrow classes of compounds? Why might it be especially suitable as a survey technique for hazardous waste sites? What is ELISA?
19. In what sense is the TCLP a measure of available toxicants?
20. What device is employed to make a nondispersive infrared analyzer selective for the compound being determined?
21. Suggest how mass spectrometry would be most useful in air pollutant analysis.
22. If 0.250 g of particulate matter is the minimum quantity required for accurate weighing on a Hi-Vol sampler filter, how long must such a sampler be operated at a flow rate of 2.00 m^3/min to collect a sufficiently large sample in an atmosphere containing 5 µg/m^3 of particulate matter?
23. Assume that the signal from a chemiluminescence analyzer for NO is proportional to NO concentration. For the same rate of air flow, an instrument gave a signal of 135 microamp for an air sample that had been passed over a thermal converter and 49 µamp with the converter out of the stream. A standard sample containing 0.233 ppm NO gave a signal of 80 µamp. What was the level of NO_2 in the atmospheric sample?
24. An atmosphere contains 0.10 ppm by volume of SO_2 at 25°C and 1.00 atm pressure. Considering the gas laws presented in Chapter 2, what volume of air would have to be sampled to collect 1.00 mg of SO_2 in tetrachloromercurate solution?

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25. Assume that 20% of the surface of a membrane filter used to collect particulate matter consists of circular openings with a uniform diameter of 0.45 μm. How many openings are on the surface of a filter with a diameter of 5.0 cm?

26. Some atmospheric pollutant analysis methods have been used in the past that later have been shown to not give the "true" value. In what respects can such methods still be useful?

27. Suggest how ion chromatography can be used for the analysis of nonionic gases.

28. Personnel monitoring in the workplace is commonly practiced with vapor samplers that workers carry around. How does this differ from biological monitoring? In what respects is biological monitoring superior?

29. Why is blood arguably the best kind of sample for biological monitoring? What are some of the disadvantages of blood in terms of sampling and sample processing? What are some disadvantages of blood as a matrix for analysis? What are the advantages of urine? Discuss why urine might be the kind of sample most likely to show metabolites and least likely to show parent species.

30. Distinguish among the following kinds of analytes measured for biological monitoring: parent compound, Phase 1 reaction product, Phase 2 reaction product, adducts.

31. What is wet ashing? For what kinds of analytes is wet ashing of blood commonly performed? What kinds of reagents are used for wet ashing, and what are some of the special safety precautions that should be taken with the use of these kinds of reagents for wet ashing?

32. What species is commonly measured potentiometrically in biological monitoring?

33. Compare the analysis of Phase 1 and Phase 2 metabolic products for biological monitoring. How are Phase 2 products converted back to Phase 1 metabolites for analysis?

34. Name a biomolecule that is commonly involved in the formation of adducts for biological monitoring. What is a simple inorganic species that can be determined as an adduct?

35. What is a use of immunology in biological monitoring? What is a disadvantage of immunological techniques? Discuss the likelihood that immunological techniques will find increasing use in the future as a means of biological monitoring.

36. The determination of DNA adducts is a favored means of measuring exposure to carcinogens. Based upon what is known about the mechanism of carcinogenicity, why would this method be favored? What might be some limitations of measuring DNA adducts as evidence of exposure to carcinogens?

37. How are mercapturic acid conjugates formed? What special role do they play in biological monitoring? What advantage do they afford in terms of measurement?

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38. For what kinds of xenobiotics is trichloroacetic acid measured? Suggest the pathways by which these compounds might form trichloroacetic acid metabolically.

39. Match each xenobiotic species from the column on the left below with the analyte that is measured in its biological monitoring from the column on the right.

A. Methanol	1. Mandelic acid
B. Malathion	2. A diketone
C. Styrene	3. Organic phosphates
D. Nitrobenzene	4. Formic acid
E. *n*-Heptane	5. *p*-Nitrophenol

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